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THE STUDY OF RING-OPENING METATHESIS POLYMERISATIONS OF STRAINED BICYCLIC MONOMERS MEDIATED BY WELL-DEFINED RUTHENIUM COMPLEXES

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Abstract

When 7-alkoxynorbornadiene monomers are subjected to Ring-Opening Metathesis Polymerisations (ROMP) mediated by $RuCl_2(PCy_3)_2(=CHPh)$ (**A**), regeneration of the initiator is observed. As the steric bulk of the 7-alkoxy functionality is decreased the extent of regeneration observed decreases accordingly (7-tert-butoxy: 27 %, 7-isopropoxy: 18 %, 7-ethoxy: 8 %, 7-methoxy: 3 %). The initial monomer to initiator ratio ($[M]_o/[I]_o$) was also found to effect the extent of regeneration. The ROMP of bicyclic olefin monomers containing oxygen functionality in positions other than the bridgehead carbon results in no regeneration of the initiator. Similarly, subtle variations to the chemistry of the ligands of initiator **A** result in no regeneration being observed, possibly due to the electronic effects of the ligands on the metal centre.

Two propagating alkylidene species are apparent in ^1H NMR spectra during the ROMP of monomer **1** mediated by initiator **A**, their identity is revealed by the addition of either free phosphine or a phosphine scavenger (CuCl) to the system once the polymerisation reaches completion. The resonance appearing as a triplet at 19.36 ppm is assigned to the alkylidene protons of bisphosphine species, whereas a broad resonance at ~17.5 ppm is assigned to a monophosphine species in which oxygen contained within the propagating polymer backbone chelates to the ruthenium centre. The latter species is stable in solution, and active for ROMP. Comparison are drawn between this species and $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)$ (**F**), a stable ruthenium complex containing internal oxygen chelation, and NMR experiments reveal that they are similar in structure. The ligand exchange and ROMP behaviour of initiator **F** is also studied.

A new methodology which permits the recovery of ruthenium alkylidene complexes from ROMP systems mediated by initiator **A** is described. The regenerated complexes are recovered in good yields and successfully employed in subsequent olefin metathesis reactions. This novel approach of induced regeneration is of significant interest due to the simple addition of terminating agents to ROMP reactions resulting in expensive non-recyclable ruthenium initiators being converted into cost effective recyclable catalysts.

Acknowledgements

Firstly, I would like to acknowledge Ezat Khosravi for his guidance, support and encouragement over the last three years, and also for providing me with the opportunity to undertake postgraduate study at the University of Durham. My sincere thanks go to the departmental NMR team; the frequent thought provoking, and often challenging, conversations with Alan Kenwright coupled with the patience and willingness of Catherine Heffernan, has contributed significantly to this work. I am also grateful to all of the technical staff in the department for their assistance and advice over the last three years.

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Memorandum

The work reported in this thesis has been carried out at the Interdisciplinary Research Centre in Polymer Science and Technology, Department of Chemistry, Durham University between June 2002 and June 2005. This work has not been submitted for any other degree either in Durham or elsewhere and is the original work of the author except where acknowledged by means of appropriate reference.

Statement of Copyright

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Analytical Data

Abbreviations

br.	broad
3-BrPyr	3-bromopyridine
^{t}Bu	*tert*-butyl
C_6D_6	deuterated benzene
$CDCl_3$	deuterated chloroform
CD_2Cl_2	deuterated dichloromethane
CM	cross metathesis
d	doublet
DCPD	dicyclopentadiene
dd	doublet of doublets
δ	chemical shift
Et	ethyl
eV	electron volts
g	grams
GPC	gel permeation chromatography
Hz	Hertz
$[I]_o$	initial concentration of initiator
IMes	1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
$IMesH_2$	1,3-bis(2,4,6-trimethylphenyl)imidazolidinylidene
J	coupling constant
k_i	rate of initiation
kJ	kilo Joules
k_p	rate of propagation
NMR	nuclear magnetic resonance
$[M]_o/[I]_o$	ratio of the initial concentrations of monomer to initiator
MALDI-TOF	matrix assisted laser desorption ionisation – time of flight
m	multiplet
mbar	millibar
Me	methyl
mg	milligram
MHz	mega Hertz
mL	millilitre
mM	millimolar

mmol	millimole
mol	mole
MS	mass spectroscopy
M_n	number average molecular weight
M_w	weight average molecular weight
m/z	mass to charge ratio
NOE	nuclear overhauser experiment
O^tBu	*tert*-butoxy
OEt	ethoxy
PCy_3	tricyclohexylphosphine
PCy_2Ph	dicyclohexyl(phenyl)phosphine
PDI	polydispersity index
PEG	polyethylene glycol
Ph	phenyl
PPh_3	triphenylphosphine
ppm	parts per million
P^iPr_3	tri-isopropylphosphine
P^iPr_2Ph	di-isopropyl(phenyl)phosphine
^iPr	*iso*-propyl
PS–DVB	polystyrene divinylbenzene
q	quartet
RCM	ring-closing metathesis
ROMP	ring-opening metathesis polymerisation
R_{pol}	polymer chain
s	singlet
sx	sextet
t	triplet
THF	tetrahydrofuran
TMS	tetramethylsilane
µg	microgram
µmol	micromole

Chapter 1

Introduction

1.1 Aims, Objectives and Overview

The primary aim of this work is to establish the parameters which govern the process of regeneration of the initiator observed during particular Ring Opening Metathesis Polymerisation (ROMP) reactions of bicyclic olefin monomers mediated by well-defined ruthenium complexes.

This chapter highlights the background science associated with this work, and the field of olefin metathesis is introduced followed by a detailed description of ROMP. In general, only information relevant to the work described in this thesis is discussed in detail, information on related topics can be found in the cited literature references.

1.2 Olefin Metathesis

1.2.1 Definition and Historic Background

Olefin metathesis is a powerful reaction that is used extensively in organic[1] and polymer[2] chemistry. It is a catalytically induced bond reorganisation process, which provides an effective pathway to the redistribution of carbon-carbon double bonds.[2] For acyclic olefins, this leads to exchange of alkylidene units (*Figure 1.1*).

Figure 1.1. General reaction scheme for the metathesis of acyclic olefins

The reaction was first reported by Banks and Bailey in 1964 and termed 'olefin disproportionation'.[3] They described a new catalytic process in which linear olefins were converted to homologues of both shorter and longer carbon chains. Catalysts such as molybdenum hexacarbonyl, tungsten hexacarbonyl and molybdenum oxide supported on alumina were employed. It was found that propene could be disproportionated to ethene and *n*-butenes (*Figure 1.2*).

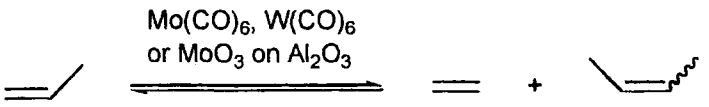


Figure 1.2. Acyclic olefin disproportionation as demonstrated by Banks and Bailey

Peters and Evering also disclosed 'disproportionation' effects via a patent.[4] But, it was not until 1972 that Calderon identified that these apparently distinct processes were examples of one and the same reaction, which he referred to as 'olefin metathesis'.[5-7]

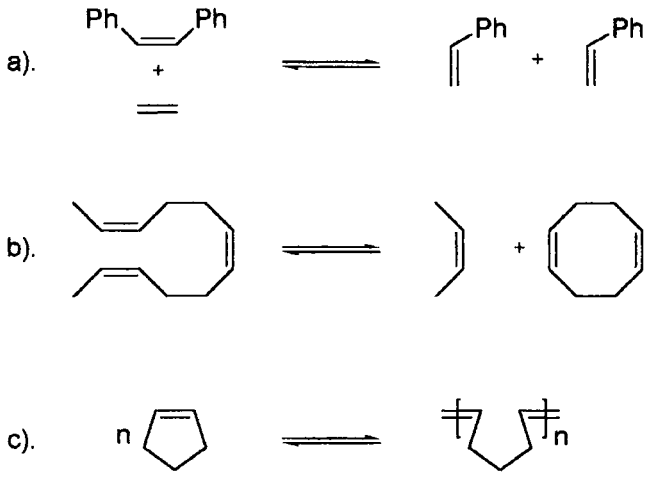


Figure 1.3. Examples of, a) Cross Metathesis, b) Ring Closing Metathesis and c) Ring Opening Metathesis Polymerisation

The metathesis reaction can be applied to all types of olefinic compounds, and the field of olefin metathesis is now categorised into three broad groups; Cross Metathesis (CM) of acyclic alkenes,[8] Ring Closing Metathesis (RCM) of acyclic dienes,[9-11] and Ring Opening Metathesis Polymerisations (ROMP) of cyclic olefins (*Figure 1.3*).[2] It has also found application in the synthesis of natural products.[12-14]

The ability to cleave and reform double bonds in new arrangements is an attractive synthetic tool for chemists. Over the course of the thirty or so years since its discovery, olefin metathesis has received widespread attention and has developed into a powerful technique for both polymer and organic synthesis.

1.2.2 General Mechanism

Bradshaw's 'pair-wise' mechanism suggested that two double bonds came together in the vicinity of the transition metal site and that the orbitals of the transition metal overlapped with those of the double bonds in such a way as to allow exchange to occur via a weakly held cyclobutane type complex.[15]

In 1971, Herisson and Chauvin proposed the now widely accepted mechanism for olefin metathesis.[16] They realised that a metal-alkylidene species (an initiator) needs to be generated in order for olefin metathesis to occur. The olefinic carbon-carbon double bond reacts with this metal alkylidene-species in a reversible [2+2] cyclo-addition, to form a metallacyclobutane species. The four-membered ring can then open either non-productively (degeneratively) to regenerate the original reagents, or productively to form a new olefin and a new metal alkylidene species (*Figure 1.4*).

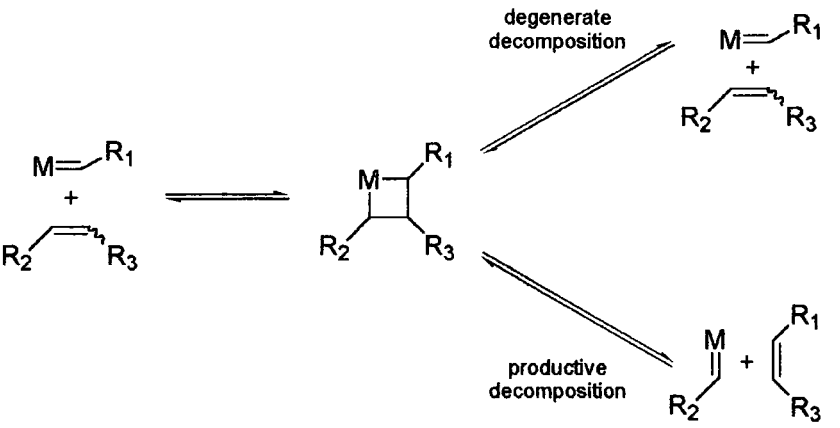


Figure 1.4. The mechanism of olefin metathesis as proposed by Herisson and Chauvin

This mechanism was more feasible than previous suggestions because metal-alkylidenes and metallacyclobutanes were known to exist. The proposal required no unusual theoretical explanations and it accounts for all the known facts about olefin metathesis. All of the above steps are reversible, therefore the outcome of CM of acyclic alkenes and RCM of acyclic dienes are dependent on reaction conditions, such as temperature, concentration, reaction duration and the nature of the substrates.

1.3 Ring Opening Metathesis Polymerisation (ROMP)

The focus of this thesis is the ROMP of norbornene and norbornadiene derivatives, which result in ring scission and the formation of unsaturated linear polymers. The first example of this type of metathesis reaction (only recognised as such some years later) was reported in a DuPont patent by Anderson and Merckling in 1955.[17] Norbornene was polymerised using a mixture of titanium tetrachloride and ethylmagnesium bromide (*Figure 1.5*). In contrast to addition polymerisation

reactions known at the time, the product was found to contain a high degree of unsaturation.

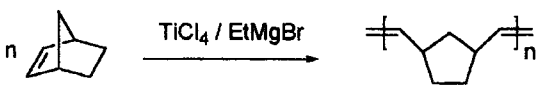


Figure 1.5. The first example of ring opening to form unsaturated polymers

1.3.1 Mechanism

For ROMP, the olefins which undergo double bond redistribution are usually strained cyclic, bicyclic or multicyclic monomers. Productive cleavage of the metallacyclobutane species formed when cyclic olefins undergo [2+2] cyclo-addition with metal-alkylidenes, leads to ring opening of the olefin which results in the formation of an unsaturated linear polymer (*Figure 1.6*).

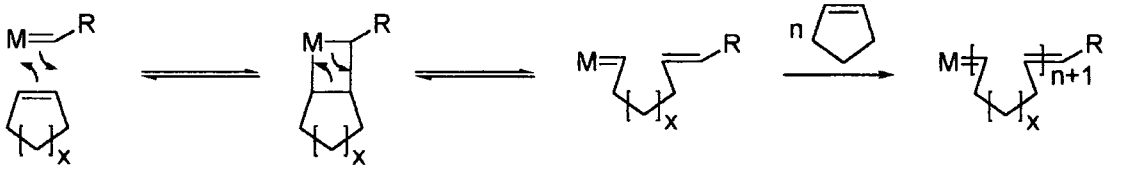


Figure 1.6. The mechanism for the ROMP of strained cyclic olefins

The high ring strain in norbornene and norbornadiene derivatives, means that the reactions are not reversible and the polymerisations go to completion. In some cases, secondary metathesis reactions, between the metal-alkylidene and double bonds contained within the polymer backbone, can occur intra- and/or intermolecularly. This broadens the molecular weight distribution of the polymer and induces the formation of cyclic oligomers.

1.3.2 Microstructure of Polymers Prepared by ROMP

The microstructure of polymers synthesised using ROMP can be quite complex and has been subject to significant study.[2] The way in which a monomer unit incorporates into a polymer chain determines the polymeric microstructure,[18-21] i.e. the frequency and distribution of the isomeric repeat units. There are four main factors that define the microstructure of polymers formed during the ROMP of norbornene or norbornadiene derivatives.[22]

1.3.2.1 *Cis/Trans* Isomerism of Vinylene Units

The backbone of polymers prepared by ROMP contain unsaturated bonds that can be in either a *cis* or *trans* configuration (*Figure 1.7*). The ratio and the distribution of *cis* and *trans* vinylene units in a polymer is dependant on the monomer, the initiator and in some cases other conditions like the solvent, concentration and temperature.[2] In practice, by the careful selection of the initiator system / conditions employed, it is possible to prepare unsaturated polymers with *cis/trans* distributions varying from all *cis* to all *trans*.[23-25]

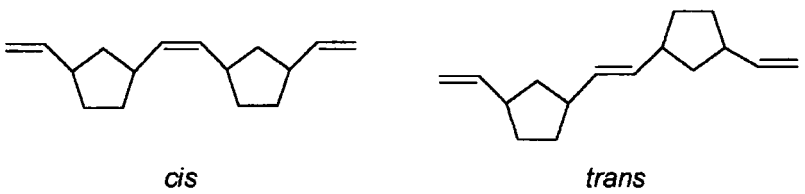


Figure 1.7. The distribution of cis and trans double bonds in polynorbornenes

1.3.2.2 Tacticity Affects

Not all norbornene and norbornadiene type monomers are necessarily chiral, but polymers from which they are formed contain tertiary carbon atoms that exhibit chirality, hence introducing tacticity effects into the polymer backbone.[2,26] Upon polymerisation, there is the possibility that the two tertiary carbon atoms either side of a double bond will have the same or different chirality, giving rise to a *racemic* or *meso* dyad, respectively.

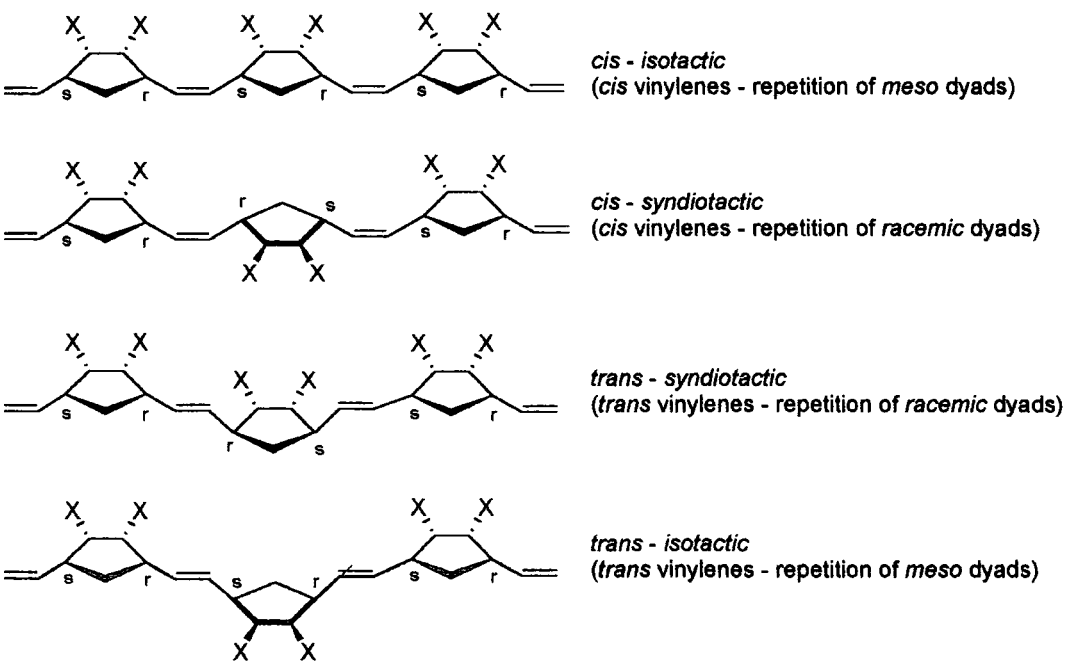


Figure 1.8. The four possible microstructural arrangements of poly(5,6-norbornenes)

Sequences of *racemic* dyads produce *syndiotactic* polymers, whereas sequences of *meso* dyads give *isotactic* polymers. Polymers with random distributions of *meso* and *racemic* dyads are *atactic*. The combination of *meso* and *racemic* dyads with *cis* and *trans* isomerism leads to four possible regular microstructural arrangements (*Figure 1.8*).

1.3.2.3 Degree of Head/Tail, Head/Head and Tail/Tail Insertion

The insertion of asymmetric monomer units, such as 5-substituted norbornenes, into propagating polymer chains gives rise to the possibility of head/tail (HT), head/head (HH) and tail/tail (TT) configurations (*Figure 1.9*). The combination of all insertion orientations gives rise to 16 possible microstructural outcomes. Some combinations of monomer and initiator have been found to give a particular bias for one form of addition.[2]

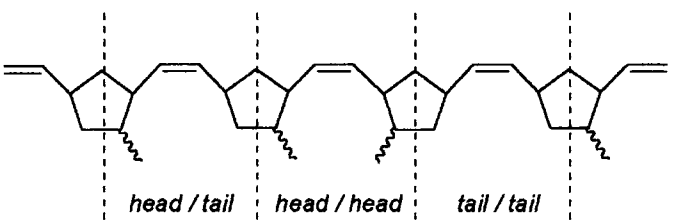


Figure 1.9. Head/tail insertion effects for polymerisation of asymmetric monomers

1.3.2.4 *Syn/Anti* Insertion of Norbornadiene Derivatives

When derivatives of norbornene type monomers are subjected to ROMP, there is only one double bond which can be opened, whereas for the ROMP of norbornadiene derivatives there are two double bonds which can potentially react with the active species. For 7-substituted norbornadienes, either the *syn* or *anti* double bond can react, thus affecting the microstructure of the polymer backbone (*Figure 1.10*).

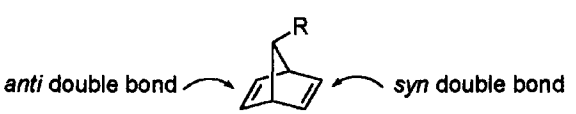


Figure 1.10. The syn and anti double bonds of 7-substituted norbornadienes

It has been demonstrated that different initiator systems / conditions give rise to varying amounts of *syn* and *anti* enchainment.[27,28]

1.3.3 Thermodynamic Aspects of ROMP

For any reaction to occur the change in the Gibbs Free Energy (ΔG) must be ≤ 0. This change is expressed as a function of the change in enthalpy (ΔH), the change in entropy (ΔS) and an absolute temperature (T / K).

$$\Delta G = \Delta H - T\Delta S$$

In all polymerisations the entropy change (ΔS) is negative since many monomer units combining to form macromolecules, results in a loss of freedom.[22] A negative value of ΔS makes the entropy term ($-T\Delta S$) positive. Therefore, for a favourable reaction, the change in enthalpy (ΔH) must be larger than the $T\Delta S$ component. The temperature at which $\Delta G=0$ ($T=\Delta H/\Delta S$), is called the ceiling temperature, above which the polymerisation cannot take place.

In general, the most favourable conditions for the ROMP of cyclic olefins are high monomer concentration, low temperature and high pressure. The change in enthalpy (ΔH) is dependent on the ring strain. Therefore, for three and four membered rings, which are highly strained due to the deformation of the normal bond angles, and rings containing eight or more carbon atoms which are strained due to torsional or transannular effects, the enthalpy change is high (i.e. negative) and polymerisations go to completion at normal temperatures and monomer concentrations. For monomers with low ring strain (5, 6 and 7 membered rings) the reaction entropy is a major determining factor, since the reaction enthalpy is low. Although norbornene and norbornadiene type monomers are composed of five and six membered rings, the strain energy (100 kJ/mol) is comparable to that of cyclopropane (115 kJ/mol).[29] This is due to distortions of bond angles around the bridgehead and, in the case of norbornenes, the ring hydrogens eclipse due to the confinement of the six membered ring to a boat conformation (*Figure 1.11*).[22]

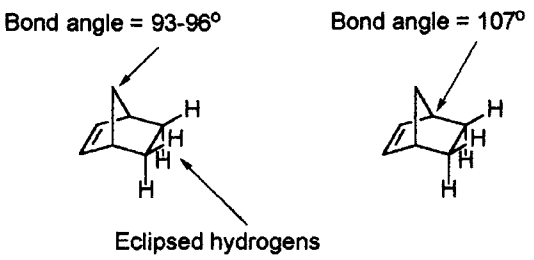


Figure 1.11. The distorted bond angles of norbornene results in high strain energy

All of the strain energy within a norbornene unit can be released by breaking any of its carbon-carbon bonds, and this is achieved during ROMP reactions. ROMP of functionalised norbornene derivatives have a reduced tendency to undergo secondary metathesis (backbiting) reactions due to steric hindrance of pendant functional groups shielding the double bonds of the polymer backbone.

1.4 Metathesis Initiators

As described above (Section 1.2.2), in order for metathesis of olefinic substrates to occur, a metal-alkylidene component is required to induce the formation of metallacyclobutane intermediates via [2+2] cyclo-addition reactions. These species, initiators, are most commonly based on groups 4 to 9 of the transition metals, and in particular, Mo, W, Re and Ru complexes are found to be useful.

Metathesis initiators are classified in two categories. These are the ill-defined 'classical initiators', and the more recently developed single component 'well-defined initiators'. The following section provides a brief summary of classical initiators and an in depth description of well-defined initiators. Directly relevant to the work in this thesis are ruthenium initiators, and in particular ROMP initiated by $RuCl_2(PCy_3)_2(=CHPh)$, which is discussed in detail.

1.4.1 Ill-Defined Classical Initiators

These initiator systems are so named because the precise nature of the active site at the metal centre is not known, and is formed *in situ* prior to reaction. Therefore, neither the number, nor the type of active metal centres present in the system can be established.

Classical initiator systems can be homogeneous or heterogeneous and are usually based on chlorides, oxides or oxychlorides of transition metals.[2] A co-catalyst is required to activate the systems, and this is normally an organometallic compound or a Lewis acid. Sometimes a third component, a promoter, is also required. The promoter is often an oxygen containing species. The classical homogeneous catalytic systems include $WCl_6/EtAlCl_2/EtOH$, $WOCl_4/Me_4Sn$ and $ReCl_5/Et_3Al/O_2$.[7] Whereas the heterogeneous supported catalyst systems include MoO_3/Al_2O_3, WO_3/SiO_2, and ReO_7/Al_2O_3.

The activity and efficiency of a classical initiator system is unpredictable and it can depend dramatically on the chemical, thermal and mechanical history of the components as well as the order and rate of mixing of the catalyst, co-catalyst and substrate. Ill-defined systems of this type suffer from a number of disadvantages. One being that only a small percentage of the catalyst forms the active species, and once generated, these active sites are usually highly reactive resulting in a fast rate of propagation, therefore giving poor control over the properties of the resulting polymer. This lack of control over molecular weight and molecular weight distribution is further compounded by the occurrence of intra- and/or intermolecular backbiting reactions. The utility of the classic systems is limited by the harsh conditions and strong Lewis acids that are required, rendering them incompatible with most functional groups.[30] An overall lack of control and reproducibility is encountered when using these classical systems, rendering them very difficult synthetic tools to work with. However, despite their shortcomings, these catalytic systems do find applications both in industry[31,32] and academia,[33] due to their low cost and simple preparation.

1.4.2 Well-Defined Metathesis Initiators

Well-defined initiators have proved to be more successful in the field of olefin metathesis than their classical counterparts. In contrast to ill-defined initiators, the exact nature of the active site of single component well-defined initiators is fully understood. Olefin metathesis reactions mediated by these transition metal alkylidene complexes are reproducible, due to the chemical identity and the concentration of active species in the system being precisely known. The arrival of well-defined initiators has dramatically increased the range of application of the olefin metathesis reaction. It is now possible to perform living ROMP and control the polymer molecular weight distribution and tacticity (Section 1.4.4).

In 1964, Fischer *et al.* isolated the first stable metal-carbene species (*Figure 1.12*).[34] The heteroatom stabilised complex was found to be reactive towards highly strained cyclic olefins such as cyclobutene and norbornene derivatives. The diphenyl complex, synthesised by Casey and Burkhardt in 1973, was not stabilised by a heteroatom and was found to be much more reactive.[35] It is able to initiate the polymerisation of less strained olefins. Although both these complexes are active well-defined initiators, they do not give rise to living polymerisations.

Fischer carbene Casey carbene

Figure 1.12. Early examples of isolated metal-carbene species

In the early 1980's, Grubbs and co-workers isolated well-defined metallacyclobutane complexes, which were active as metathesis initiators. The reaction of Tebbe's reagent with various olefins in the presence of nitrogen bases resulted in the formation of titanacyclobutane complexes (*Figure 1.13*).[36,37] It has been shown that these species readily exchange with olefins via a rate determining loss of the olefin from the titanacyclobutane ring to generate the transition metal methylidene species $Cp_2Ti{=}CH_2$, which is active for metathesis. The polymerisation proceeds without termination or chain transfer to give polynorbornene with a narrow molecular weight distribution.[38]

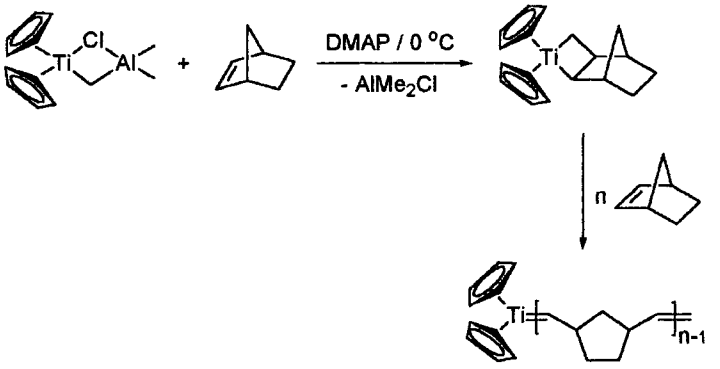


Figure 1.13. Conversion of Tebbe reagent into a titanocyclobutane initiator and its subsequent use in the living ROMP of norbornene

This was the first well-documented example of a living polymerisation of a cyclic olefin, and it was a significant step forward in the development of ROMP initiators. However, the system did have its drawbacks, the titanacyclobutanes must be heated to 50 °C in order to ring-open even norbornenes, and the highly electrophilic nature of the metal centre makes them very reactive towards any functionality contained within the monomer. The discovery of this type of olefin metathesis initiator increased interest in well-controlled living ROMP, and was followed by the development of well-defined initiators based upon molybdenum, tungsten, and tantalum.[39-44]

Schrock and co-workers introduced well-defined tungsten and molybdenum initiators with bulky alkoxide and arylimido ligands of the type $M(CHR)(NAr)(OR')_2$ (*Figure 1.14*). The sterics of these complexes allow relatively small substrates to attack the metal carbene and form five co-ordinate intermediate metallacyclobutane complexes. The bulky alkoxide groups and the imido ligand prevent dimerisation of the metal centres, which could result in inactive bimetallic complexes or decomposition of the complex. The introduction of electronegative trifluoromethyl groups on the alkoxy ligands makes the complexes more active, due to the reduction of the electron density on the metal centre rendering it more electrophilic and a better 'acceptor' for incoming olefins.[45] This effect is neatly demonstrated by the observation that when OR` = $OC(CH_3)(CF_3)_2$ the tungsten complex will readily metathesise acyclic olefins, whereas when OR` = O^tBu no such reaction occurs.

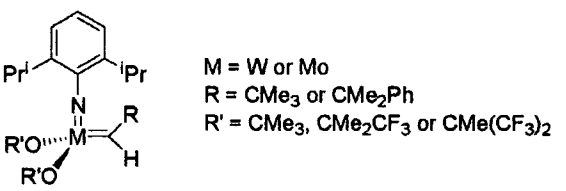


Figure 1.14. Well-defined Schrock initiators

The fluorinated Mo type catalysts react rapidly with olefins and are able to perform ROMP on low-strained monomers, as well as ring-closing of sterically demanding and electron-poor substrates. However, these catalysts, and others based on early transition metals, are limited by the high oxophilicity of the metal centres, which render them extremely sensitive to oxygen and moisture. As a result of this, they are limited by their moderate/poor functional group tolerance, which reduces the scope of potential substrates.[45]

1.4.3 Ruthenium Alkylidene Initiators

The focus of this thesis is the ROMP of bicyclic olefin monomers mediated by well-defined ruthenium initiators. In this section, the development of ruthenium complexes that have found application in the field of ROMP is outlined, and particular attention is paid to $RuCl_2(PCy_3)_2(=CHPh)$[46] (Grubbs 1st generation initiator), and $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)$[47] (Hoveyda's initiator), which are used extensively in the work reported herein.

Table 1.1. Functional group tolerance of well-defined olefin metathesis initiators [a]

Titanium	Tungsten	Molybdenum	Ruthenium
Acids	Acids	Acids	**Olefins**
Alcohols, Water	Alcohols, Water	Alcohols, Water	Acids
Aldehydes	Aldehydes	Aldehydes	Alcohols, Water
Ketones	Ketones	**Olefins**	Aldehydes
Esters, Amides	**Olefins**	Ketones	Ketones
Olefins	Esters, Amides	Esters, Amides	Esters, Amides

[a] The metal at the top of each column is able to tolerate the functional groups that appear below '**olefins**'

The functional group tolerance of ruthenium complexes is found to be better relative to early transition metal complexes such as; titanium, tungsten and molybdenum, and this is the main reason that interest in their use as olefin metathesis initiators, especially in the last ten years, has been so intense.[48] This trend is shown in *Table 1.1*, where well-defined initiators based on the metal at the top of the column are able to tolerate the functional groups appearing below '**olefins**' in each column.

Titanium and tungsten initiators are inclined to react with ketones and esters, whereas molybdenum initiators are more reactive toward olefins, although they also react with aldehydes and other polar or protic groups. Ruthenium complexes react preferentially with carbon-carbon double bonds over most other functionalities, which make these initiators unusually stable toward alcohols, amides, aldehydes, and carboxylic acids. Therefore, metathesis initiators based on ruthenium increase the functional group tolerance and hence increase the scope of monomers that can be successfully subjected to ROMP.

Ruthenium-based complexes were not considered to be particularly suitable metathesis catalysts until the early 1980's. The main reasons being that ruthenium salts exhibited a low metathesis activity, and there was a limited understanding of how functional group tolerance could be best achieved. The first indication that complexes based on ruthenium may be useful was when the activity of $RuCl_3$(hydrate) was studied. It was found to have very long initiation periods under strictly anhydrous conditions, but water was found not only to be compatible with the catalyst system, but also beneficial to the initiation process. The polymerisation could

be conducted in aqueous solution.[49,50] Other ruthenium complexes, such as $Ru(H_2O)_6(tos)$ (tos = p-toluenesulfonate), were found to have initiation rates of a few minutes,[51] and this particular initiator was able to ROMP functionalised norbornene derivatives generating polymers in greater yields, higher molecular weights and lower polydispersities than most other initiators known at that time. However, the initiation process remained unclear, but it was believed that ruthenium alkylidene species were the active component. Although no ruthenium alkylidene species at that time were known to be able to perform olefin metathesis, the success found with other transition metal alkylidene complexes led to research being heavily focused on the pursuit for a metathesis active ruthenium alkylidene complex.

1.4.3.1 1st Generation Ruthenium Initiators

In 1992, Grubbs and co-workers reported a major breakthrough. They synthesised $RuCl_2(PPh_3)_2(=CHCH=CPh_2)$ and found it could polymerise norbornene and other highly strained cyclic olefins, in a living fashion.[52] The complex was prepared via reaction of either $RuCl_2(PPh_3)_3$ or $RuCl_2(PPh_3)_4$ with diphenylcyclopropene (*Figure 1.15*). These reactions resulted in stable 16 electron bis(phosphine) ruthenium alkylidene complexes that were active for the polymerisation of norbornene and stable in the presence of protic solvents.

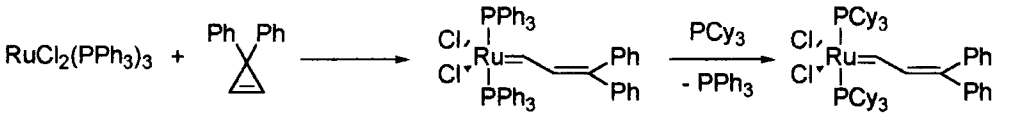


Figure 1.15. The synthesis of ruthenium alkylidene initiators from 3,3-phenylcyclopropane

It was found that, $RuCl_2(PPh_3)_2(=CHCH=CPh_2)$ was only active for metathesis with strained and electron rich olefins and peculiarly, it would not polymerise *cis*-cyclooctene although it would polymerise *trans*-cyclooctene. In order to increase the activity of this initiator, ligand exchanges were performed. Firstly, the reaction of $RuCl_2(PPh_3)_2(=CHCH=CPh_2)$ with $Ag(OOCCF_3)$ led to the two chlorine atoms being replaced with trifluoroacetate groups.[53] The resulting complex is an active olefin metathesis initiator, although like its dichloro analogue it is only reactive towards olefins with a high level of ring strain.

The relationship between the halogen atoms contained within ruthenium complexes and their activity for olefin metathesis was studied (*Table 1.2*).[54] Initiators with bromine ligands were noticeably less active than their chlorine analogues, and replacement of the chlorine ligands with iodine results in complexes with very low or even no olefin metathesis activity.

It was established that substitution of the PPh_3 ligands with more basic PCy_3 ligands, leads to a substantial increase in activity of the initiator, which permits the ROMP of unstrained cyclic olefins and metathesis of acyclic olefins.[46,55,56] The activity of the initiator decreases in the following order of phosphine ligands: PCy_3 > P^iPr_3 > PCy_2Ph > P^iPr_2Ph. The larger, more basic (electron donating) phosphines appear to increase activity, and the complex in which chlorine is combined with PCy_3, is found to have the highest activity. Indeed, these ruthenium-based complexes are able to promote many of the same reactions as the molybdenum-based alkylidene complexes reported by Schrock, but have a greater functional group tolerance and can be handled using standard organic techniques.[57] The early transition metal-based initiators require vacuum line and dry box conditions if they are to be used efficiently, whereas this type of ruthenium initiator can be handled in air (as solids) and the reactions, if desired, can be carried out under a nitrogen atmosphere in standard flasks.

Table 1.2. Relative activities of initiators of the type $RuX_2(PR_3)_2(=CH\text{-}CH=CPh_2)$ for the RCM of diethyl diallymalonate

PR_3	X	Activity (turnovers/h)
PCy_3	Cl	19.0
	Br	15.4
	I	1.4
PCy_2Ph	Cl	8.0
	Br	4.5
	I	[a]
P^iPr_3	Cl	17.5
	Br	13.9
	I	1.1
P^iPr_2Ph	Cl	5.5
	Br	2.3
	I	[a]

[a] Initiator showed no signs of activity for the reaction even after several hours.

Although these complexes are very attractive for olefin metathesis and their preparation via the cyclopropene route is convenient on the gram scale, it is difficult to scale-up the reactions. In 1996, it was reported that complexes of this type could be prepared by the use of diazo compounds.[46] This was found to be an excellent route towards stable ruthenium complexes, and was extended to the preparation of ruthenium benzylidene complexes (*Figure 1.16*).

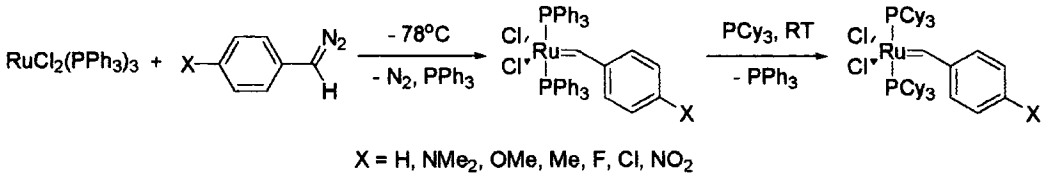


Figure 1.16. Synthesis of ruthenium alkylidene complexes with diazo compounds

This family of initiators have high activity and rapid initiation rates when employed in olefin metathesis reactions, and these complexes have served as the basis for the recent developments in ruthenium metathesis technology.[46,58]

When used to mediate the ROMP of strained cyclic olefins, these initiators are capable of producing polymers which are nearly monodisperse (PDI = 1.04-1.20) and they fulfill the general criteria for a living system, since the propagating alkylidene is stable throughout the reaction, and the molecular weights of the polymers display a linear dependence on the [initiator]/[monomer] ratio (Section 1.4.4).[59]

Ruthenium complexes of the type $RuX_2(PR_3)_2(=CHR)$, are most commonly referred to as Grubbs 1st generation initiators. The relative rates of initiation and propagation for ROMP of strained cyclic olefins using these complexes can be easily deduced, by observation of the characteristic resonances for the alkylidene proton of the initiator and the respective propagating species by ^1H NMR as the polymerisation proceeds. These complexes do have one major drawback, in that they exhibit low thermal stability and readily decompose when subjected to elevated temperatures.[60] Despite this, $RuCl_2(PCy_3)_2(=CHPh)$, in particular has found wide spread use in all aspects of olefin metathesis, and it is this initiator that receives greatest attention in this thesis. A more extensive look at the properties and characteristics of this complex when used to initiate living ROMP is described in Section 1.4.4.

1.4.3.2 2nd Generation Ruthenium Initiators

Recent work by Grubbs,[61] Hermann[62,63] and Nolan[64] increased the scope of the ruthenium family of complexes by the preparation of initiators coordinated with unsaturated and saturated substituted *N*-mesityl imidazole ligands, $RuCl_2(PCy_3)(IMes)(=CHPh)$ and $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$, respectively (*Figure 1.17*). These complexes exhibit high RCM activity and display dramatically improved thermal stability and inertness towards oxygen and moisture compared to $RuCl_2(PCy_3)_2(=CHPh)$. These types of complexes are referred to as Grubbs 2nd generation initiators.

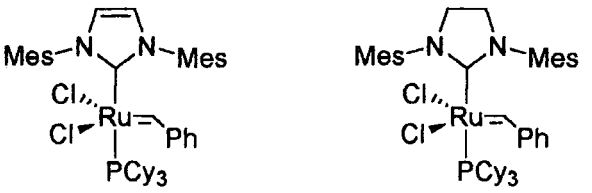


Figure 1.17. Ruthenium-based initiators coordinated with unsaturated (IMes) and saturated ($IMesH_2$) N-mesityl substituted imidazole ligands

The imidazole ligand of $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$ is more basic than that of $RuCl_2(PCy_3)(IMes)(=CHPh)$ due to a lack of carbene stabilisation provided by π-interactions. The ruthenium alkylidene is therefore more electron rich, and hence the catalytic activity in RCM and CM of $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$ not only exceeds that of $RuCl_2(PCy_3)(IMes)(=CHPh)$, but also begins to rival that of Schrock-type molybdenum complexes, while maintaining the functional group compatibility of $RuCl_2(PCy_3)_2(=CHPh)$. More interestingly, it is found that both $RuCl_2(PCy_3)(IMes)(=CHPh)$ and $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$ are more active than molybdenum complexes for ROMP. The imidazole ligand is believed to play two important roles; firstly it is a better electron donor than PCy_3, therefore enhancing the initiators' activity towards olefins, and secondly, it is more sterically demanding than PCy_3 which helps prevent (or slow) bimolecular decomposition reactions.[60]

The high activity of $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$ coupled with its high functional group tolerance has resulted in it becoming a very useful and popular tool for organic synthesis, being used in both RCM[65] and CM[66] reactions. Additionally, the initiator is capable of performing the ROMP of norbornene and norbornadiene derivatives at very fast rates. Unfortunately the rate of propagation is usually far higher than that of

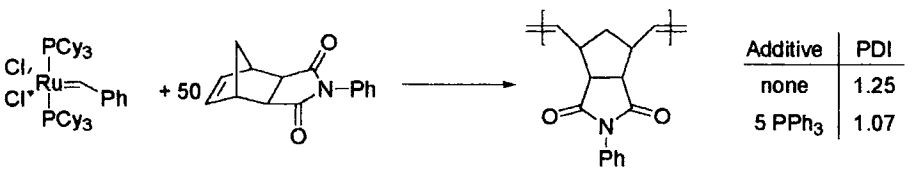
initiation (^{1}H NMR spectroscopy indicates that generally, less than 5% of the complex initiates before the ROMP of the monomer reaches completion), and backbiting may also occur to some degree.[67] Thus in more extreme cases polymers with very high and broad molecular weights are obtained.[68]

Although, $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$ is not found to be particularly useful for the ROMP of strained cyclic monomers, compared to $RuCl_2(PCy_3)_2(=CHPh)$, it has proved useful in entropically driven polymerisation of large ring systems,[69] and it can be effective for the polymerisation of macromolecular monomers. The high steric hindrance present in macromonomers can, in some cases, hinder ROMP initiated by $RuCl_2(PCy_3)_2(=CHPh)$ resulting in slow and incomplete polymerisation.[67] But this steric hindrance becomes beneficial for polymerisations initiated by $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$ because it lowers k_p relative to k_i and suppresses chain transfer reactions, resulting in well-controlled polymerisations.[70]

With a few exceptions, it is generally accepted that Grubbs 2nd generation initiators are not an appropriate choice for mediating the ROMP of most monomer systems. It is also important to note that the widespread use of $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$ is limited by its relatively difficult preparation. The synthesis utilises the free carbene, which is extremely air and moisture sensitive. Once generated, it can be directly trapped by $RuCl_2(PCy_3)_2(=CHPh)$, but isolation of the new complex requires oxygen free, anhydrous conditions and multiple purifications to remove the free phosphine generated during the synthesis.

1.4.3.3 3rd Generation Ruthenium Initiators

As described above, when $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$ is used to mediate ROMP of cyclic olefins, the high value of k_p relative to k_i results in uncontrolled polymerisation processes, and the resultant polymers have high molecular weights and broad molecular weight distributions. The addition of free phosphines to ROMP reactions mediated by $RuCl_2(PCy_3)_2(=CHPh)$ is found to improve the relative rates of k_i and k_p and give more controlled polymerisation (*Figure 1.18*),[70] but this was not found to be the case for $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$.



Additive	PDI
none	1.25
5 PPh_3	1.07

Figure 1.18. Improving the polydispersity by the addition of phosphines when using $RuCl_2(PCy_3)_2(=CHPh)$ as the initiator of ROMP

However, whilst examining the rates of ligand loss during mechanistic studies of $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$, it was found that bispyridine derivatives could be easily formed, and that they exhibit very high ligand exchange rates. These derivatives employ two pyridine ligands in place of one PCy_3 ligand (*Figure 1.19*). The higher number of ligands in initiators of this type relative to $RuCl_2(PCy_3)_2(=CHPh)$, is attributed to the lower steric bulk of the pyridine ligands compared to PCy_3.[71]

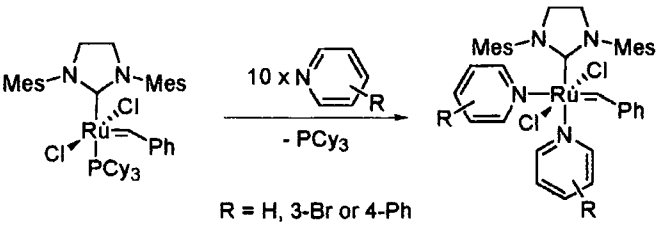


Figure 1.19. Synthesis of 3rd generation ruthenium complexes

The pyridine ligands are found to exchange in excess of 100 times faster than PCy_3, and the reactivity of these complexes can be tuned by the use of substituted pyridines. The use of 3-bromopyridine (3-BrPyr) as the ligands results in an initiator which exhibits optimum levels of reactivity, and this '3rd generation initiator' appears to retain the functional group tolerance reported for $RuCl_2(PCy_3)_2(=CHPh)$.[72]

Complex, $RuCl_2(IMesH_2)(3\text{-}BrPyr)_2(=CHPh)$ is a highly active initiator for ROMP, and in contrast to $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$, the polymerisations exhibit much higher values of k_i relative to k_p. It is found that polymerisation of norbornene mediated by $RuCl_2(IMesH_2)(3\text{-}BrPyr)_2(=CHPh)$ at room temperature produces polymer with a relatively broad molecular weight distribution (PDI =1.65), but by reducing the temperature to -20 °C it was lowered to just 1.08. The thermal stability of the initiator is not particularly good, which limits its use in organic synthesis.

As well as being used to initiate the ROMP of a variety of norbornene derivatives producing polymers with narrow polydispersities, the formation of well-controlled block copolymers by $RuCl_2(IMesH_2)(3\text{-}BrPyr)_2(=CHPh)$ is also permitted. Quenching the polymerisation with ethyl vinyl ether either before or after the addition of the second monomer, results in homo and block copolymers, respectively, being recovered with narrow molecular weight distributions (*Figure 1.20*).[72,73]

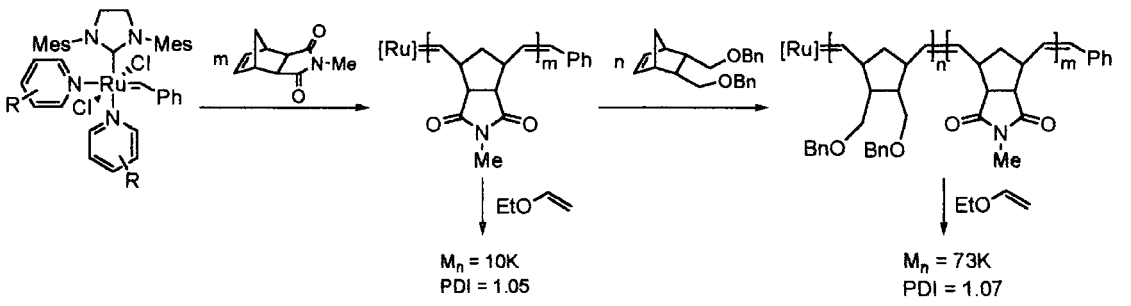


Figure 1.20. The synthesis of well-defined homo- and blockco-polymers using 3rd generation ruthenium initiators

It is evident that polymerisation reactions initiated by $RuCl_2(IMesH_2)(3\text{-}BrPyr)_2(=CHPh)$ are living from its use in the synthesis of well-defined block copolymers by sequential addition of norbornene monomers. The multiblock copolymers possess narrow PDI's and there is no evidence of homopolymers or unreacted blocks.[73]

Systematic studies examining the effect of changing the chemical nature of the pyridine ligands of these initiators, and their performance in ROMP, have not yet been published. However it seems highly likely that these 3rd generation initiators will find extensive use in synthesis of ROMP polymers in the future.

1.4.4 The Mechanism of Living ROMP Mediated by Ruthenium Initiators

A living polymerisation is a chain polymerisation that proceeds in the absence of termination or chain transfer reactions. Consequently, once the monomer has been consumed, the propagating polymer chain end remains active. There are some important features of living polymerisations:[74]

- The polymerisation proceeds until all of the monomer has been consumed, and further addition of monomer results in continued polymerisation.

- The number average molecular weight (M_n) is a linear function of conversion and thus the molecular weight can be controlled by the stoichiometry of the reaction.
- The number of active centres remains constant and is independent of conversion
- The resultant polymers have narrow molecular weight distributions
- Block copolymers can be prepared by sequential addition of monomers
- Chain-end functionalised polymers can be prepared by the appropriate choice of initiators and terminating agents.

When well-defined ruthenium complexes are employed to mediate the ROMP of strained bicyclic monomers, the reactions are considered to be living. ROMP is a chain growth polymerisation, and proceeds via three distinct steps; initiation, propagation and termination. $RuCl_2(PCy_3)_2(=CHPh)$ is widely used to mediate ROMP reactions, and the mechanism by which each step occurs is established.[75,76] Additionally, each step can be followed by ^1H NMR spectroscopy.

1.4.4.1 Initiation

It is established that PCy_3 dissociates from $RuCl_2(PCy_3)_2(=CHPh)$ to enable the double bond of the monomer unit to react with the ruthenium-carbon double bond via a [2+2] cyclo-addition reaction to form a metallacyclobutane species. Degenerative cleavage of this four-membered ring results in the formation of the original reactants, whereas productive cleavage (initiation) results in the formation of a new alkylidene species, called the propagating alkylidene (*Figure 1.21*).

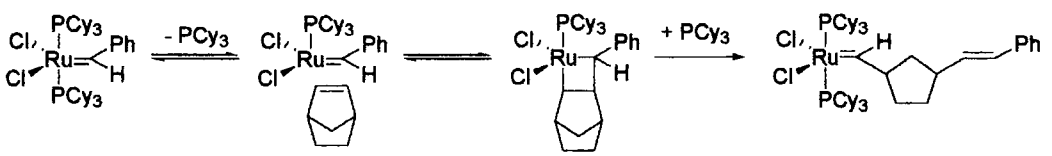


Figure 1.21. The initiation step using $RuCl_2(PCy_3)_2(=CHPh)$ for ROMP

The process of initiation can be clearly seen by ^1H NMR spectroscopy as the characteristic alkylidene proton resonance of the initiator (19.99 ppm) is converted into propagating alkylidene resonances, which typically appear between 19.5 and 18.0

ppm. The exact chemical shift and multiplicity of the propagating species is dependent on the nature of the inserted monomer unit.

1.4.4.2 Propagation

The insertion of subsequent monomer units into the active polymer chain-end is known as the propagation step. The monomer units insert via a [2+2] cyclo-addition reaction, which results in extending the length of the propagating polymer chain and consumption of the monomer (*Figure 1.22*). The rate of consumption of the monomer can be obtained by analysis of the vinylic region of ^{1}H NMR spectra as the reaction proceeds. The 'sharp' olefinic resonances of the monomer diminish as the 'broad' polymeric olefinic resonances increase in intensity.

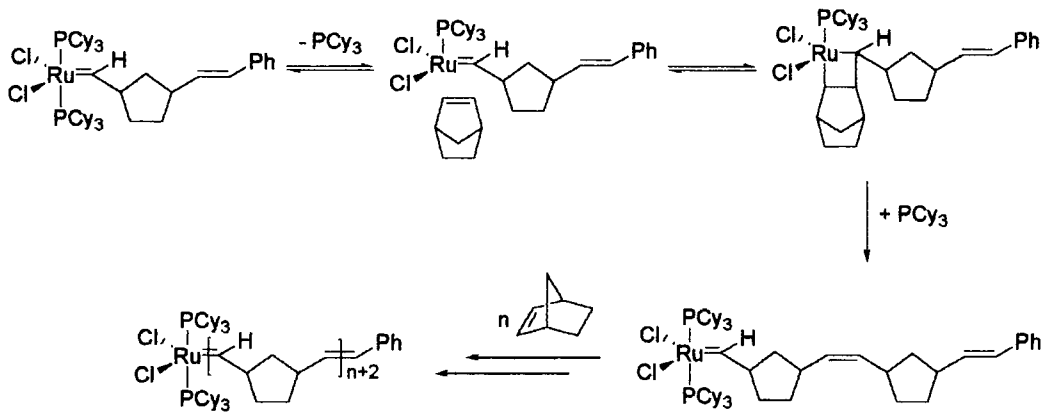


Figure 1.22. The propagation step using $RuCl_2(PCy_3)_2(=CHPh)$ for ROMP

1.4.4.3 Termination

Once the monomer has been completely consumed, the propagating alkylidene species remain active in solution. If desired, a subsequent batch of a second monomer can be added to form a block copolymer, or the reaction can be terminated by the addition of an acyclic olefinic terminating agent. For ROMP reactions mediated by $RuCl_2(PCy_3)_2(=CHPh)$, the most commonly used terminating agent is ethyl vinyl ether. Reaction of propagating ruthenium alkylidene species with ethyl vinyl ether results in almost exclusive formation (98 %) of $RuCl_2(PCy_3)_2(=CHOEt)$ and CH_2 end-capped polymer (*Figure 1.23*). Termination can be observed by ^{1}H NMR spectroscopy as the protons of the propagating alkylidene species disappear and the only alkylidene species present in the system is $RuCl_2(PCy_3)_2(=CHOEt)$ (14.58 ppm).

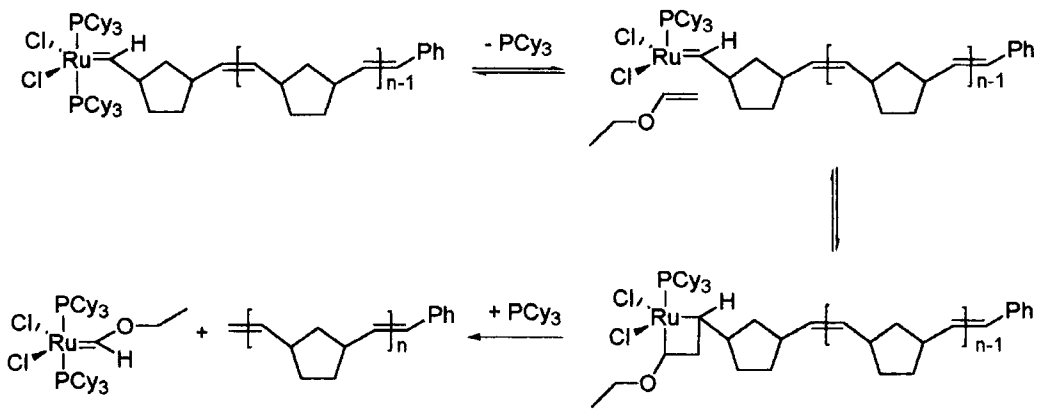


Figure 1.23. The termination step using $RuCl_2(PCy_3)_2(=CHPh)$ for ROMP

1.4.4.4 Pathway to decomposition for $RuCl_2(PCy_3)_2(=CHPh)$

It is established that the concentration of $RuCl_2(PCy_3)_2(=CHPh)$, and propagating species there of, remain almost constant during initiation and propagation of a typical ROMP reaction (typically < 10 hours).[60] However, if $RuCl_2(PCy_3)_2(=CHPh)$ (and related ruthenium benzylidene complexes) are left in solution over an extended time period they decomposes via a bimetallic pathway.[60,77] When dissolved in benzene at 55 °C $RuCl_2(PCy_3)_2(=CHPh)$ is found to have a half-life of 8 days. The pathway to decomposition is believed to occur by the coupling of two mono(phosphine) species $[RuCl_2(PCy_3)(=CHR)]$ which undergo reaction to form inorganic products and the corresponding alkene (RHC=CHR) (*Figure 1.24*).[60]

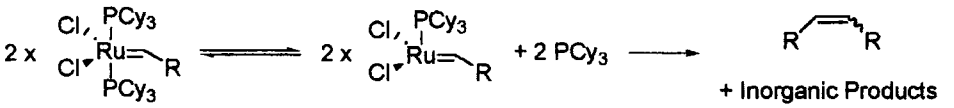


Figure 1.24 The pathway to decomposition for ruthenium alkylidene complexes $[RuCl_2(PCy_3)_2(=CHR)]$

This mechanism is supported by the quantitative appearance of olefinic resonances in ^1H NMR spectra coinciding with the disappearance of the ruthenium alkylidene proton resonance. As expected, the build-up of free phosphine generated as the decomposition progresses is found to inhibit the rate of formation of the mono(phosphine) species and hence retard the rate of decomposition.[75,76] This effect is most significant at the early stages of decomposition, where the changes in phosphine concentration are highest.[60] When decomposition was carried out in the presence of free PCy_3 the rate of decomposition was significantly retarded.

Conversely, in the presence of CuCl (a phosphine 'sponge', which enhances the formation of the mono(phosphine) species) the half-life of $RuCl_2(PCy_3)_2(=CHPh)$ was just 10 minutes at 55°C in benzene.[60]

1.4.5 Modified 1st and 2nd Generation Ruthenium Initiators

Several modifications of $RuCl_2(PCy_3)_2(=CHPh)$ have been reported, with the aim of obtaining better reactivity, or simply to adapt the complex to suit a specific catalytic condition.[78]

Sulphur containing analogues of $RuCl_2(PCy_3)_2(=CHPh)$, and mono(phosphine) ruthenium alkylidene complexes containing intramolecular coordinating pyridyl ligands have been reported (*Figure 1.25*).[79,80] They are prepared by either a one-pot procedure from $RuCl_2(COD)$ via a ruthenium hydride species, or CM between $RuCl_2(PCy_3)_2(=CHPh)$ and the corresponding aryl vinyl thioether or 2-(3-butenyl)pyridine. Both types of catalyst are able to polymerise DCPD with a lower catalyst concentration than required for analogous polymerisations mediated by $RuCl_2(PCy_3)_2(=CHPh)$. Therefore, this results in lowering the extent of ruthenium contaminants contained within the product. Polymerisations mediated by the pyridyl containing complexes are thermally activated. This is convenient for handling of the DCPD/catalyst formulation prior to reaction injection molding.

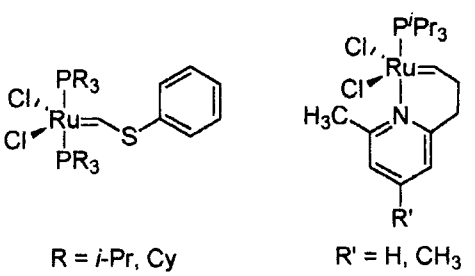


Figure 1.25. Sulphur and pyridyl containing ruthenium alkylidene complexes

The introduction of Schiff base ligands to $RuCl_2(PCy_3)_2(=CHPh)$ was performed independently by Grubbs[81] and Verpoort[82] to give complexes of the type shown in *Figure 1.26.* These complexes are highly stable to air, moisture, and elevated temperatures and even exhibit catalytic activity for RCM and ROMP in polar protic solvents such as methanol and ionic liquids.

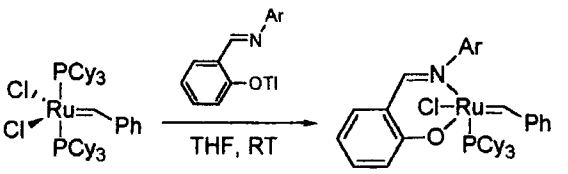


Figure 1.26. The introduction of Schiff base ligands to $RuCl_2(PCy_3)_2(=CHPh)$

Substitution of the PCy_3 ligands of $RuCl_2(PCy_3)_2(=CHPh)$ with water soluble phosphines allows the preparation of complexes which are able to initiate the ROMP of functionalised 7-oxanorbornenes and RCM reactions in water, methanol, and aqueous emulsions (*Figure 1.27*).[83-87]

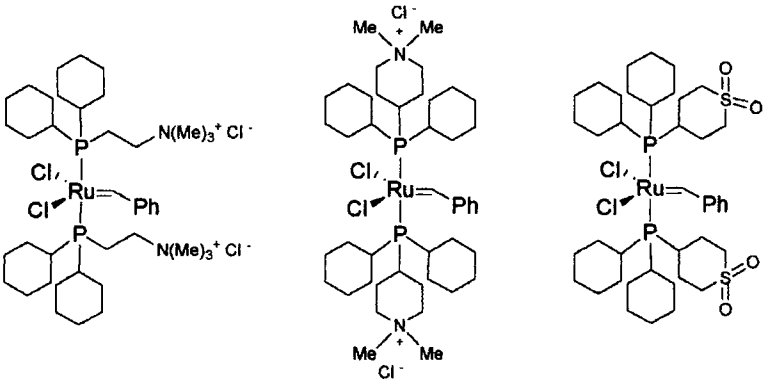


Figure 1.27. Examples of water soluble analogues of $RuCl_2(PCy_3)_2(=CHPh)$

During the catalytic cycle of olefin metathesis mediated by $RuCl_2(PCy_3)_2(=CHPh)$ a phosphine ligand dissociates from the metal centre to form the active 14 electron complex.[54] With the aim of obtaining more efficient initiators, Grubbs replaced the two halide ligands of $RuCl_2(PCy_3)_2(=CHPh)$ with tertiary alkoxides, which possess π-donor abilities, and synthesised the four coordinate, 14-electron ruthenium alkylidene complexes (*Figure 1.28*). These compounds, which were isolated and studied by X-ray crystallography, were found to be active metathesis initiators, capable of ring-closing diethyl diallylmalonate with yields up to 96 %.[88]

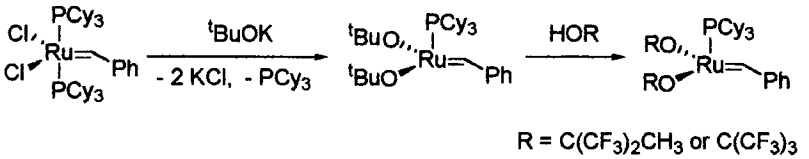


Figure 1.28. Four coordinate, 14-electron ruthenium alkylidene complexes

Hoveyda described the synthesis of substituted benzylidene analogues of 1st and 2nd generation ruthenium initiators which are highly efficient for olefin metathesis (*Figure 1.29*).[47,89] The complexes contain internal oxygen chelation to the ruthenium centre.

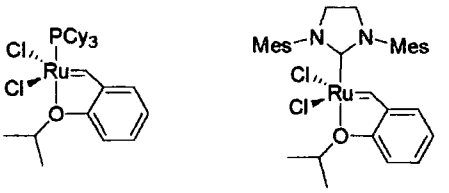


Figure 1.29. Hoveyda type well-defined ruthenium complexes

Like the previously described initiators they possess high tolerance to functional groups, and they have enhanced stability towards molecular oxygen. This has led to their widespread use in organic synthesis.[89] When employed to mediate the ROMP of strained cyclic olefins, this type of initiator produces polymers with polydispersities significantly broader than those of corresponding polymers prepared by $RuCl_2(PCy_3)_2(=CHPh)$.[90] However, of particular interest to this thesis is the observation that the characteristic alkylidene proton resonance of $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)$ is observed at 17.44 ppm in NMR spectra, and also that it appears as a doublet due to coupling with the phosphorous nucleus of the PCy_3 ligand.

1.4.6 Methods for Initiator Recovery / Recycling via Immobilisation

Polymer immobilised reagents have been extensively used in organic chemistry[91] and recently it has become clear that olefin metathesis reactions, especially RCM, are best carried out under conditions where the initiator can be easily separated from the products of the reaction.[92-97] Immobilisation of olefin metathesis initiators by attaching them to insoluble polymeric supports offers significant advantages over homogeneous metathesis systems. Firstly, the extent of contamination of the product with metallic residues can be considerably reduced, this is especially important in the field of pharmaceutical chemistry. The removal of ruthenium based initiators and their decomposition products from homogeneous olefin metathesis reactions is tedious and time consuming, particularly with polymeric products.[98] Secondly, well-defined single component olefin metathesis initiators are expensive, and contribute significantly to the total cost of the final product. Therefore their regeneration or re-

use, both achievable by immobilisation, is highly desirable. And finally, supported catalysis offers access to high-throughput techniques and continuous flow reactors.

There are four major considerations that need to be addressed when attaching olefin metathesis initiators to polymeric supports:

1. It is important to preserve the high activities and reaction rates observed with the corresponding homogeneous initiators,
2. The initiator must be easily separated from the reaction mixture,
3. It is desirable if the initiator can be recycled and preferably used in multiple reactions,
4. The olefin metathesis products must be free from metallic contaminants.

This section highlights the recent advances that have been made in the immobilisation of ruthenium alkylidene complexes. There are four established techniques by which ruthenium species, of the type $RuX_2L_2(=CHR)$, can be attached to polymeric supports; via exchange of either a) phosphines, b) the alkylidene, c) halogens, or d) the N-heterocyclic carbene (*Figure 1.30*).

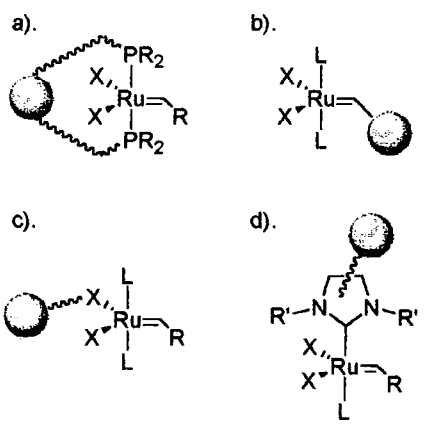


Figure 1.30. The four established techniques by which ruthenium complexes can be attached to polymeric supports

1.4.6.1 Immobilisation via Phosphine Exchange

Ruthenium-based olefin metathesis initiators can be supported on phosphine functionalised, low-crosslinked (2 %) polystyrene divinylbenzene (PS–DVB) resins via exchange between the phosphines of the initiator and the support. The first example of this type of support was reported by Grubbs *et al.* in 1995, who

demonstrated that complexes of the type $RuCl_2(PR_3)_2(=CHCH=CPh_2)$ could be successfully immobilised (*Figure 1.31*).[99]

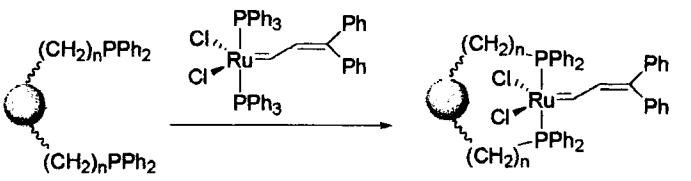


Figure 1.31. Immobilisation of $RuCl_2(PPh_3)_2(=CHCH=CPh_2)$ on phosphine functionalised supports

Unfortunately, the supported initiator showed significantly reduced activity for the ROMP of norbornene relative to the 'free' initiator. This loss in activity was attributed to incomplete substitution of phosphines coupled with problems of leaching. Verpoort *et al.* used a similar approach to immobilise $RuCl_2(PCy_3)_2(=CHPh)$ on a phosphine fuctionalised mesoporous silica support.[100] Not unexpectedly, the ROMP of norbornene using this support resulted in polymer with broad polydispersities (up to 7.2) and it was found to have very low RCM activity.

1.4.6.2 Immobilisation via Alkylidene Exchange

Ruthenium alkylidene complexes are known to undergo cross metathesis with acyclic olefins,[46] and this methodology has been employed as a technique to attach them to polymeric supports. When these types of supports are used to mediate olefin metathesis reactions, the active ruthenium centre is either cleaved from the support (in the case of CM and RCM) or is attached to the support via a polymeric backbone (in the case of ROMP) (*Figure 1.32*).

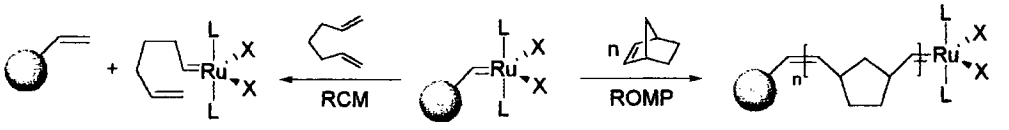


Figure 1.32. The use of ruthenium initiators supported via the alkylidene ligand for RCM and ROMP

For CM and RCM, the idea of a supported initiator acting in solution and returning to the support once all the substrate has been consumed, is certainly attractive, and these

type of supported catalyst systems have been named 'boomerang' catalysts (*Figure 1.33*).[101]

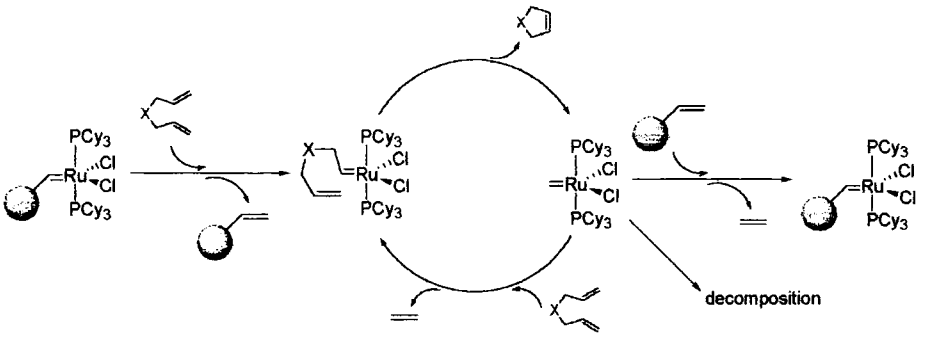


Figure 1.33. The mechanism by which 'boomerang' initiators perform RCM

However, their use is limited by continuous decomposition of the initiator which occurs whilst it is 'unbound' in solution. This prevents complete re-attachment to the support once the reaction reaches completion, resulting in two problems. Firstly, the use of the supported initiator for multiple olefin metathesis reactions is limited by the extent of leaching of the active centres, and secondly, this 'leaching' results in the products being contaminated with high levels of ruthenium. However, improvements have been made, and the extent of leaching is found to be reduced by a factor of 10 when 2nd generation ruthenium initiators [$RuCl_2(PCy_3)(IMes)(=CHPh)$ and $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$] are attached to supports in place of $RuCl_2(PCy_3)_2(=CHPh)$.[102-104] This type of support finds no application in the field of ROMP if the polymer needs to be recovered from the reaction mixture, because polymerisation results in the product being chemically bound to the support (*Figure 1.32*).

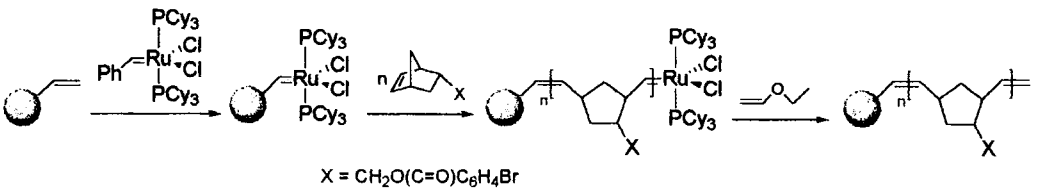


Figure 1.34. Synthesis of poly(norbornene)-loaded supports for use in combinatorial chemistry

However, Barrett *et al.* describe that poly(norbornene) loaded supports find use in combinatorial chemistry. These supports can be synthesised via the reaction of

$RuCl_2(PCy_3)_2(=CHPh)$ supported on PS-DVB with substituted norbornenes (*Figure 1.34*).[105]

Hoveyda *et al* reported a recyclable, ruthenium-based metathesis initiator $[RuCl_2(PCy_3)(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)]$, and it became clear that immobilisation of this initiator onto a support leads to an enhancement in the efficiency of supported 'boomerang' catalysts.[47] This is due to the active ruthenium centre having an increased affinity to react with the 2-*iso*-propoxystryrenyl moiety that remains bound to the support. This type of initiator is extremely robust towards oxygen and moisture, and has been successfully supported on dendrimers,[106] polyethylene glycol (PEG)[107,108] and polystyrene[109,110] (*Figure 1.35*).

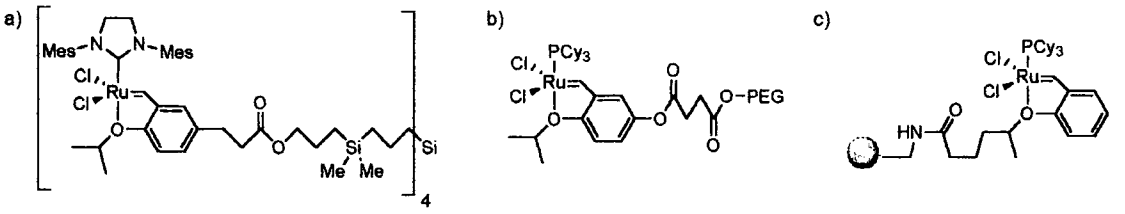


Figure 1.35. The immobilisation of Hoveyda type complexes on a) dendrimers, b) PEG polymers, and c) Aminomethyl-PS-DVB supports

These types of support exhibit significantly increased persistence in RCM, and in some cases they can be used in up to 20 cycles with the ruthenium content of the products remaining impressively low.[111]

1.4.6.3 Immobilisation via Halogen Exchange

The halogen ligands of ruthenium alkylidene initiators remain bound to the metal centre during olefin metathesis reactions, and therefore if complexes are attached to the support via substitution of these ligands the active site should remain bound to the polymeric support during the reaction. In the case of RCM and CM the reaction products should be easy to isolate from the supported initiator by filtration, and leaching of the initiator into solution should be minimal, resulting in low levels of ruthenium contamination of the product. For ROMP using this type of support, the polymer remains immobilised during the reaction, and can be cleaved by the addition of acyclic olefinic terminating agents (*Figure 1.36*).

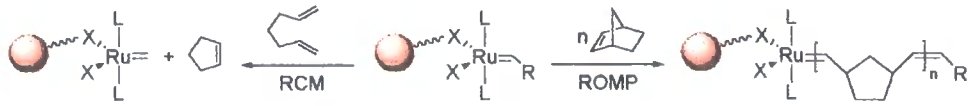


Figure 1.36. The use of ruthenium initiators supported via halogen exchange for RCM and ROMP

In 2001, Mol *et al.* reported the permanent immobilisation of a ruthenium alkylidene complex to a PS–DVB-support. $RuCl_2(PCy_3)_2(=CHPh)$ was attached to the support via substitution of one of its chlorine ligands with a fluorinated ester linkage (*Figure 1.37*).[112] The support was found to be active for CM and RCM reactions, although a decrease in activity was observed during consecutive cycles. The support was easily separated from the reaction products, which were almost free from ruthenium contaminants.

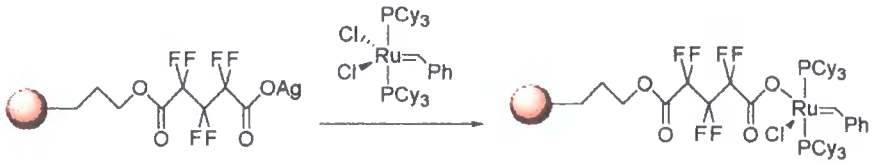


Figure 1.37. Immobilisation of a ruthenium alkylidene complex to a PS–DVB-support via halogen exchange

Buchmeiser *et al*, prepared a monolith-supported 2nd generation Grubbs initiator $[RuCl_2(PCy_3)(IMesH_2)(=CHPh)]$ by a similar procedure, which as expected, were highly active for RCM reactions (*Figure 1.38*).[113] In addition, numerous supported variations of Hoveyda-type initiators $[RuCl_2(IMesH_2)(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)]$ were synthesised. Interestingly, the exchange of chlorine with strongly electron-withdrawing groups of the support enhance the reactivity of these systems without compromising their high stability, and the extent of leaching was found to be low (*Figure 1.38*).[114]

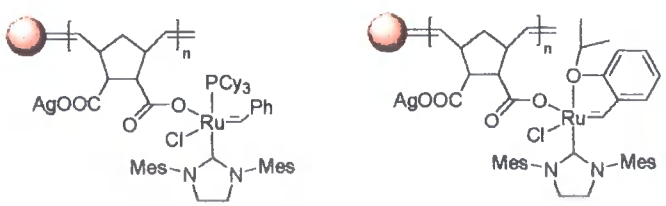


Figure 1.38. Monolith-bound 2nd generation complexes based on dicarboxylates

1.4.6.4 Immobilisation via the N-Heterocyclic Carbene

2nd generation ruthenium alkylidene complexes can be attached to supports through their N-heterocyclic carbene ligands. This methodology provides advantages over immobilisation of complexes via phosphine exchange, because the mechanism of olefin metathesis does not involve dissociation of N-heterocyclic carbene ligands, and hence there should be a reduction in the extent of leaching observed.

The first ruthenium based metathesis initiator immobilised via the N-heterocyclic carbene was reported by Blechert *et al.*[115] They reacted $RuCl_2(PCy_3)_2(=CHPh)$ with an $IMesH_2$ functionalised PS–DVB support in order to generate the immobilised initiator (*Figure 1.39*). This support was successfully used in RCM and was easy to handle. They also supported the Hoveyda version of this type of initiators, which resulted in improved recyclability of the support (*Figure 1.38*).[116]

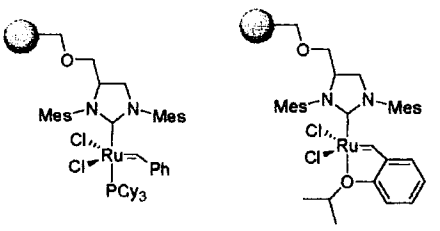


Figure 1.39. PS-DVB-supported 2nd generation ruthenium initiators

Other research groups have immobilised ruthenium alkylidene complexes onto ROMP derived monoliths[117,118] and silica supports[119,120] via substitution of the N-heterocyclic carbene ligands with various substituted analogues.

1.5 Summary of the Work Reported in this Thesis

It has previously been shown that when the well defined ruthenium complex, $RuCl_2(PCy_3)_2(=CHPh)$, is used to mediate the ROMP of 7-*tert*-butoxynorbornadiene using $[M]_o/[I]_o = 50$, the reaction exhibits remarkable behaviour.[28,121] Analysis of the alkylidene region of the ^1H NMR spectra obtained during the reaction reveals that, over a 24 hour period, the initiator is regenerated at the expense of the propagating species as the reaction proceeds.[121] This is believed to occur by intra- or inter-molecular secondary metathesis reactions at the living chain ends of the propagating polymer chains.[28] A broad alkylidene resonance (X) is also observed and it slowly increases in intensity as the reaction proceeds, and it is extremely stable in solution.

The observation of regeneration of the initiator during the ROMP of 7-*tert*-butoxynorbornadiene mediated by $RuCl_2(PCy_3)_2(=CHPh)$ is the first of its kind.

The primary aim of this work in this thesis is to establish the parameters which govern the process of regeneration of the initiator observed during the ROMP of 7-*tert*-butoxynorbornadiene mediated by $RuCl_2(PCy_3)_2(=CHPh)$. The phenomenon of regeneration has been extended into new systems by methodically varying specific aspects of the system in which this unusual behaviour was observed.[122] These, and related systems, were monitored by NMR spectroscopy in order to investigate the nature of propagating species that arise during the polymerisations.[122] It was then found that by the appropriate choice of terminating agent it is possible to induce regeneration of the initiator in potentially any ROMP system mediated by well-defined ruthenium complexes.

1.6 References

1. A. Furstner, Editor, *Alkene Metathesis in Organic Synthesis. [In: Top. Organomet. Chem., 1998; 1]*, **1998**.
2. K. J. Ivin, I. C. Mol, Editors, *Olefin Metathesis and Metathesis Polymerization, Second Edition*, **1996**.
3. R. L. Banks, G. C. Bailey, *Industrial & Engineering Chemistry Product Research and Development* **1964**, *3*, 170.
4. E. F. Peters, B. L. Evering, (Standard Oil Co. (Indiana)). Us, **1960**, pp. Continuation.
5. N. Calderon, H. Y. Chen, K. W. Scott, *Tetrahedron Letters* **1967**, 3327.
6. N. Calderon, E. A. Ofstead, W. A. Judy, *Journal of Polymer Science, Polymer Chemistry Edition* **1967**, *5*, 2209.
7. N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, K. W. Scott, *Journal of the American Chemical Society* **1968**, *90*, 4133.
8. R. H. Grubbs, *Tetrahedron* **2004**, *60*, 7117.
9. A. Furstner, M. Liebl, C. W. Lehmann, M. Picquet, R. Kunz, C. Bruneau, D. Touchard, P. H. Dixneuf, *Chemistry--A European Journal* **2000**, *6*, 1847.
10. A. D. Piscopio, J. E. Robinson, *Current Opinion in Chemical Biology* **2004**, *8*, 245.
11. A. H. Hoveyda, R. R. Schrock, *Comprehensive Asymmetric Catalysis, Supplement* **2004**, *1*, 207.
12. M. A. Leeuwenburgh, G. A. van der Marel, H. S. Overkleeft, *Current Opinion in Chemical Biology* **2003**, *7*, 757.
13. D. D. Manning, X. Hu, P. Beck, L. L. Kiessling, *Journal of the American Chemical Society* **1997**, *119*, 3161.
14. S. Biagini, V. C. Gibson, M. R. Giles, E. L. Marshall, M. North, *Chemical Communications* **1997**, 1097.
15. C. P. C. Bradshaw, E. J. Howman, L. Turner, *Journal of Catalysis* **1967**, *7*, 269.
16. J. L. Herisson, Y. Chauvin, *Makromolekulare Chemie* **1971**, *141*, 161.
17. A. W. Anderson, N. G. Merckling, (E. I. du Pont de Nemours & Co.). Us, **1955**.
18. J. G. Hamilton, K. J. Ivin, J. J. Rooney, *Journal of Molecular Catalysis* **1985**, *28*, 255.
19. T. Steinhaeusler, F. Stelzer, E. Zenkl, *Polymer* **1994**, *35*, 616.

20. T. Sunaga, K. J. Ivin, G. E. Hofmeister, J. H. Oskam, R. R. Schrock, *Macromolecules* **1994**, *27*, 4043.

21. J. W. Feast, V. C. Gibson, K. J. Ivin, A. M. Kenwright, E. Khosravi, *Journal of Molecular Catalysis* **1994**, *90*, 87.

22. K. J. Ivin, T. Saegusa, *Ring-Opening Polymerisation, Vol. 1*, Elsevier Applied Science Publishers Ltd., **1984**.

23. E. Khosravi, W. J. Feast, A. A. Al-Hajaji, T. Leejarkpai, *Journal of Molecular Catalysis A: Chemical* **2000**, *160*, 1.

24. R. O'Dell, D. H. McConville, G. E. Hofmeister, R. R. Schrock, *Journal of the American Chemical Society* **1994**, *116*, 3414.

25. R. R. Schrock, *Topics in Organometallic Chemistry* **1998**, *1*, 1.

26. L. Delaude, A. Demonceau, A. F. Noels, *Macromolecules* **2003**, *36*, 1446.

27. K. J. Ivin, A. M. Kenwright, E. Khosravi, J. G. Hamilton, *Journal of Organometallic Chemistry* **2000**, *606*, 37.

28. K. J. Ivin, A. M. Kenwright, E. Khosravi, J. G. Hamilton, *Macromolecular Chemistry and Physics* **2001**, *202*, 3624.

29. P. R. Khoury, J. D. Goddard, W. Tam, *Tetrahedron* **2004**, *60*, 8103.

30. U. Frenzel, O. Nuyken, *Journal of Polymer Science, Part A: Polymer Chemistry* **2002**, *40*, 2895.

31. J. C. Mol, *NATO Science Series, II: Mathematics, Physics and Chemistry* **2003**, *122*, 313.

32. J. C. Mol, *Journal of Molecular Catalysis A: Chemical* **2004**, *213*, 39.

33. M. McCann, E. M. G. Coda, K. Maddock, *Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999)* **1994**, 1489.

34. E. O. Fischer, A. Maasboel, *Angew. Chem.* **1964**, *76*, 645.

35. C. P. Casey, T. J. Burkhardt, *Journal of the American Chemical Society* **1973**, *95*, 5833.

36. T. R. Howard, J. B. Lee, R. H. Grubbs, *Journal of the American Chemical Society* **1980**, *102*, 6876.

37. D. A. Straus, R. H. Grubbs, *Organometallics* **1982**, *1*, 1658.

38. L. R. Gilliom, R. H. Grubbs, *Journal of the American Chemical Society* **1986**, *108*, 733.

39. C. J. Schaverien, J. C. Dewan, R. R. Schrock, *Journal of the American Chemical Society* **1986**, *108*, 2771.

40. J. S. Murdzek, R. R. Schrock, *Organometallics* **1987**, *6*, 1373.

41. R. R. Schrock, J. Feldman, L. F. Cannizzo, R. H. Grubbs, *Macromolecules* **1987**, *20*, 1169.

42. R. R. Schrock, R. T. DePue, J. Feldman, C. J. Schaverien, J. C. Dewan, A. H. Liu, *Journal of the American Chemical Society* **1988**, *110*, 1423.

43. R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. DiMare, M. O'Regan, *Journal of the American Chemical Society* **1990**, *112*, 3875.

44. R. R. Schrock, R. T. DePue, J. Feldman, K. B. Yap, D. C. Yang, W. M. Davis, L. Park, M. DiMare, M. Schofield, et al., *Organometallics* **1990**, *9*, 2262.

45. R. R. Schrock, *Accounts of Chemical Research* **1990**, *23*, 158.

46. P. Schwab, R. H. Grubbs, J. W. Ziller, *Journal of the American Chemical Society* **1996**, *118*, 100.

47. J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus, Jr., A. H. Hoveyda, *Journal of the American Chemical Society* **1999**, *121*, 791.

48. T. M. Trnka, R. H. Grubbs, *Accounts of Chemical Research* **2001**, *34*, 18.

49. B. M. Novak, R. H. Grubbs, *Journal of the American Chemical Society* **1988**, *110*, 7542.

50. S. Y. Lu, P. Quayle, F. Heatley, C. Booth, S. G. Yeates, J. C. Padget, *Macromolecules* **1992**, *25*, 2692.

51. M. A. Hillmyer, C. Lepetit, D. V. McGrath, B. M. Novak, R. H. Grubbs, *Macromolecules* **1992**, *25*, 3345.

52. S. T. Nguyen, L. K. Johnson, R. H. Grubbs, J. W. Ziller, *Journal of the American Chemical Society* **1992**, *114*, 3974.

53. Z. Wu, S. T. Nguyen, R. H. Grubbs, J. W. Ziller, *Journal of the American Chemical Society* **1995**, *117*, 5503.

54. E. L. Dias, S. T. Nguyen, R. H. Grubbs, *Journal of the American Chemical Society* **1997**, *119*, 3887.

55. A. Demonceau, A. F. Noels, E. Saive, A. J. Hubert, *Journal of Molecular Catalysis* **1992**, *76*, 123.

56. S. T. Nguyen, R. H. Grubbs, J. W. Ziller, *Journal of the American Chemical Society* **1993**, *115*, 9858.

57. G. C. Fu, S. T. Nguyen, R. H. Grubbs, *Journal of the American Chemical Society* **1993**, *115*, 9856.

58. P. Schwab, M. B. France, J. W. Ziller, R. H. Grubbs, *Angewandte Chemie, International Edition in English* **1995**, *34*, 2039.

59. C. Pariya, K. N. Jayaprakash, A. Sarkar, *Coordination Chemistry Reviews* **1998**, *168*, 1.

60. M. Ulman, R. H. Grubbs, *Journal of Organic Chemistry* **1999**, *64*, 7202.

61. M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Letters* **1999**, *40*, 2247.

62. U. Frenzel, T. Weskamp, F. J. Kohl, W. C. Schattenmann, O. Nuyken, W. A. Herrmann, *Journal of Organometallic Chemistry* **1999**, *586*, 263.

63. W. A. Herrmann, M. Elison, J. Fischer, C. Koecher, G. R. J. Artus, *Angewandte Chemie, International Edition in English* **1995**, *34*, 2371.

64. J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *Journal of the American Chemical Society* **1999**, *121*, 2674.

65. L. Jafarpour, S. P. Nolan, *Journal of Organometallic Chemistry* **2001**, *617-618*, 17.

66. A. K. Chatterjee, T.-L. Choi, D. P. Sanders, R. H. Grubbs, *Journal of the American Chemical Society* **2003**, *125*, 11360.

67. S. Jha, S. Dutta, N. B. Bowden, *Macromolecules* **2004**, *37*, 4365.

68. H. D. Maynard, S. Y. Okada, R. H. Grubbs, *Macromolecules* **2000**, *33*, 6239.

69. P. Hodge, S. D. Kamau, *Angewandte Chemie, International Edition* **2003**, *42*, 2412.

70. C. W. Bielawski, R. H. Grubbs, *Macromolecules* **2001**, *34*, 8838.

71. J. A. Love, J. P. Morgan, T. M. Trnka, R. H. Grubbs, *Angewandte Chemie, International Edition* **2002**, *41*, 4035.

72. T.-L. Choi, R. H. Grubbs, *Angewandte Chemie, International Edition* **2003**, *42*, 1743.

73. C. Slugovc, S. Riegler, G. Hayn, R. Saf, F. Stelzer, *Macromolecular Rapid Communications* **2003**, *24*, 435.

74. R. P. Quirk, B. Lee, *Polymer International* **1992**, *27*, 359.

75. M. S. Sanford, J. A. Love, R. H. Grubbs, *Journal of the American Chemical Society* **2001**, *123*, 6543.

76. M. S. Sanford, M. Ulman, R. H. Grubbs, *Journal of the American Chemical Society* **2001**, *123*, 749.

77. E. L. Dias, R. H. Grubbs, *Organometallics* **1998**, *17*, 2758.

78. Y. Imamoglu, L. Bencze, *Novel Metathesis Chemistry: Well-Defined Initiator Systems for Specialty Chemical Synthesis, Tailored Polymers and Advanced Material Applications.*, **2003**.

79. P. A. van der Schaaf, R. Kolly, H. J. Kirner, F. Rime, A. Muhlebach, A. Hafner, *Journal of Organometallic Chemistry* **2000**, *606*, 65.

80. E. Khosravi, T. Szymanska-Buzar, Editors, *Ring Opening Metathesis Polymerization and Related Chemistry: State of the art and Visions for the New Century., Vol. 56*, Kluwer Academic Publishers, **2002**.

81. S. Chang, L. Jones, II, C. Wang, L. M. Henling, R. H. Grubbs, *Organometallics* **1998**, *17*, 3460.

82. B. De Clercq, F. Verpoort, *Advanced Synthesis & Catalysis* **2002**, *344*, 639.

83. D. M. Lynn, B. Mohr, R. H. Grubbs, *Journal of the American Chemical Society* **1998**, *120*, 1627.

84. B. Mohr, D. M. Lynn, R. H. Grubbs, *Organometallics* **1996**, *15*, 4317.

85. T. A. Kirkland, D. M. Lynn, R. H. Grubbs, *Journal of Organic Chemistry* **1998**, *63*, 9904.

86. D. M. Lynn, R. H. Grubbs, *Journal of the American Chemical Society* **2001**, *123*, 3187.

87. T. Roelle, R. H. Grubbs, *Chemical Communications* **2002**, 1070.

88. M. S. Sanford, L. M. Henling, M. W. Day, R. H. Grubbs, *Angewandte Chemie, International Edition* **2000**, *39*, 3451.

89. H. Hoveyda Amir, G. Gillingham Dennis, J. Van Veldhuizen Joshua, O. Kataoka, B. Garber Steven, S. Kingsbury Jason, P. A. Harrity Joseph, *Organic & biomolecular chemistry*, *2*, 8.

90. S. Demel, W. Schoefberger, C. Slugovc, F. Stelzer, *Journal of Molecular Catalysis A: Chemical* **2003**, *200*, 11.

91. M. R. Buchmeiser, *Polymeric Materials in Organic Synthesis and Catalysis*, Wiley-VCH, Weinheim, **2003**.

92. D. Semeril, H. Olivier-Bourbigou, C. Bruneau, P. H. Dixneuf, *Chemical Communications* **2002**, 146.

93. N. Audic, H. Clavier, M. Mauduit, J.-C. Guillemin, *Journal of the American Chemical Society*, *125*, 9248.

94. M. Picquet, I. Tkatchenko, I. Tommasi, P. Wasserscheid, J. Zimmermann, *Advanced Synthesis & Catalysis* **2003**, *345*, 959.

95. S. Csihony, C. Fischmeister, C. Bruneau, I. T. Horvath, P. H. Dixneuf, *New Journal of Chemistry* **2002**, *26*, 1667.

96. A. Fuerstner, L. Ackermann, K. Beck, H. Hori, D. Koch, K. Langemann, M. Liebl, C. Six, W. Leitner, *Journal of the American Chemical Society* **2001**, *123*, 9000.

97. M. R. Buchmeiser, *New Journal of Chemistry* **2004**, *28*, 549.

98. H. D. Maynard, R. H. Grubbs, *Tetrahedron Letters* **1999**, *40*, 4137.

99. S. T. Nguyen, R. H. Grubbs, *Journal of Organometallic Chemistry* **1995**, *497*, 195.

100. K. Melis, D. De Vos, P. Jacobs, F. Verpoort, *Journal of Molecular Catalysis A: Chemical* **2001**, *169*, 47.

101. M. Ahmed, A. G. M. Barrett, D. C. Braddock, S. M. Cramp, P. A. Procopiou, *Tetrahedron Letters* **1999**, *40*, 8657.

102. M. Ahmed, T. Arnauld, A. G. M. Barrett, D. C. Braddock, P. A. Procopiou, *Synlett* **2000**, 1007.

103. L. Jafarpour, S. P. Nolan, *Organic Letters* **2000**, *2*, 4075.

104. L. Jafarpour, M.-P. Heck, C. Baylon, H. M. Lee, C. Mioskowski, S. P. Nolan, *Organometallics* **2002**, *21*, 671.

105. A. G. M. Barrett, S. M. Cramp, R. S. Roberts, *Organic Letters* **1999**, *1*, 1083.

106. S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *Journal of the American Chemical Society* **2000**, *122*, 8168.

107. Q. Yao, *Angewandte Chemie, International Edition* **2000**, *39*, 3896.

108. J. Connon Stephen, S. Blechert, *Bioorganic & medicinal chemistry letters*, *12*, 1873.

109. J. Dowden, J. Savovic, *Chemical Communications* **2001**, 37.

110. K. Grela, M. Tryznowski, M. Bieniek, *Tetrahedron Letters* **2002**, *43*, 9055.

111. H. Hoveyda Amir, G. Gillingham Dennis, J. Van Veldhuizen Joshua, O. Kataoka, B. Garber Steven, S. Kingsbury Jason, P. A. Harrity Joseph, *Organic & biomolecular chemistry* **2004**, *2*, 8.

112. P. Nieczypor, W. Buchowicz, W. J. N. Meester, F. P. J. T. Rutjes, J. C. Mol, *Tetrahedron Letters* **2001**, *42*, 7103.

113. J. O. Krause, S. Lubbad, O. Nuyken, M. R. Buchmeiser, *Advanced Synthesis & Catalysis* **2003**, *345*, 996.

114. J. O. Krause, O. Nuyken, K. Wurst, M. R. Buchmeiser, *Chemistry--A European Journal* **2004**, *10*, 777.

115. S. C. Schurer, S. Gessler, N. Buschmann, S. Blechert, *Angewandte Chemie, International Edition* **2000**, *39*, 3898.

116. S. Randl, N. Buschmann, S. J. Connon, S. Blechert, *Synlett* **2001**, 1547.

117. F. M. Sinner, M. R. Buchmeiser, *Angewandte Chemie, International Edition* **2000**, *39*, 1433.

118. F. Sinner, M. R. Buchmeiser, *Macromolecules* **2000**, *33*, 5777.

119. M. Mayr, M. R. Buchmeiser, K. Wurst, *Advanced Synthesis & Catalysis* **2002**, *344*, 712.

120. S. Pruehs, C. W. Lehmann, A. Fuerstner, *Organometallics* **2004**, *23*, 280.

121. K. J. Ivin, A. M. Kenwright, E. Khosravi, *Chemical Communications* **1999**, 1209.

122. D. M. Haigh, A. M. Kenwright, E. Khosravi, *Tetrahedron* **2004**, *60*, 7217.

Chapter 2

Regeneration of the Initiator During ROMP Mediated by Well-Defined Ruthenium Complexes

2.1 Introduction

The Ring Opening Metathesis Polymerisation (ROMP) of norbornene and norbornadiene derivatives mediated by well-defined ruthenium complexes is studied. The chemical structure of the ruthenium alkylidene complexes and the bicyclic olefin monomers discussed in this chapter are depicted in *Figures 2.1* and *2.2*, respectively.

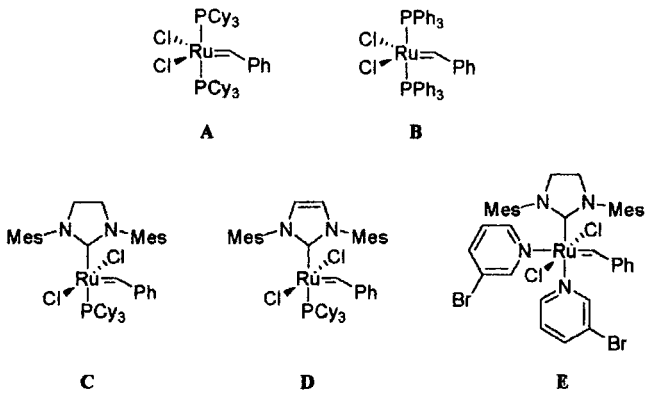


*Figure 2.1. $RuCl_2(PCy_3)_2(=CHPh)$ [**A**], $RuCl_2(PPh_3)_2(=CHPh)$ [**B**], $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$ [**C**], $RuCl_2(PCy_3)(IMes)(=CHPh)$ [**D**] and $RuCl_2(3\text{-}BrPyr)_2(IMesH_2)(=CHPh)$ [**E**]*

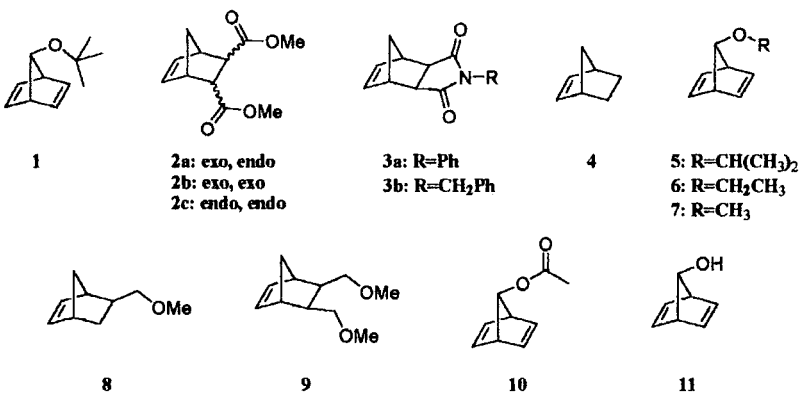


*Figure 2.2. 7-tert-butoxynorbornadiene [**1**], exo,endo-5-6-dicarbomethoxynorbornene [**2a**], exo,exo-5,6-dicarbomethoxynorbornene [**2b**], endo,endo-5-6-dicarbomethoxynorbornene [**2c**], exo-N-phenyl-5,6-dicarboxyimidonorbornene [**3a**], exo-N-phenylmethyl-5,6-dicarboxyimidonorbornene [**3b**], norbornene [**4**], 7-iso-propoxynorbornadiene [**5**], 7-ethoxynorbornadiene [**6**], 7-methoxynorbornadiene [**7**], exo-5-methoxymethylnorbornene [**8**], exo,exo-5,6-bis(methoxymethyl)norbornene [**9**], 7-acetoxynorbornadiene [**10**] and 7-hydroxynorbornadiene [**11**]*

The course of a typical ROMP reaction mediated by $RuCl_2(PCy_3)_2(=CHPh)$ (*Figure 2.1*, **A**) is described and each step of the polymerisation (initiation, propagation and termination) is monitored by ^1H NMR spectroscopy.

The phenomenon of regeneration of the initiator observed when 7-*tert*-butoxynorbornadiene (*Figure 2.2*, **1**) is subjected to ROMP mediated by initiator **A** is discussed, and the parameters which govern the regeneration process are investigated.[1-3]

2.2 Monitoring ROMP Mediated by Initiator A using ^1H NMR Spectroscopy

The use of well-defined alkylidene complexes to mediate the ROMP of strained cyclic olefins, results in a step-growth polymerisation. The mechanism of ROMP using ruthenium alkylidene species is well established and the reaction proceeds via three distinct steps: initiation, propagation and termination. Each step can be monitored by ^1H NMR spectroscopy, and the example of initiator **A** mediating the ROMP of *exo,endo*-5,6-dicarbomethoxynorbornene (*Figure 2.2*, **2a**) is described below.

2.2.1 Initiation

Prior to initiation of a ROMP reaction, characteristic resonances for both the initiator and monomer can be observed by ^1H NMR spectroscopy (*Figure 2.3*).

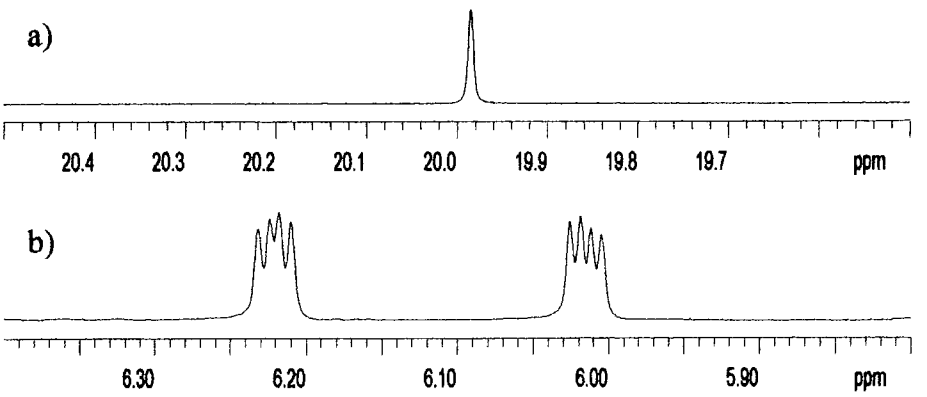


*Figure 2.3. 500 MHz ^1H NMR spectra ($CDCl_3$) of a) the alkylidene proton resonance of initiator **A**, and b) the olefinic protons of monomer **2a***

The alkylidene proton of initiator **A** gives rise to a singlet at 19.99 ppm, and the olefinic protons of monomer **2a** appear as multiplets between 6.3 and 6.0 ppm.

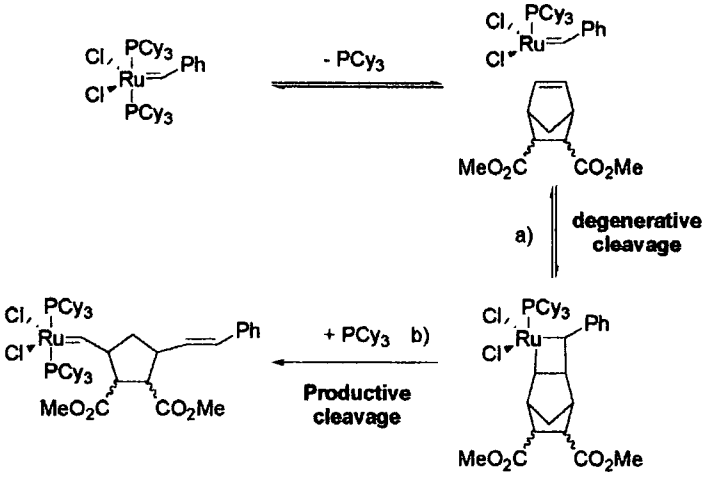


*Figure 2.4. The process of initiation using initiator **A** to mediate ROMP*

The process of initiation occurs by dissociation of a PCy_3 ligand from the ruthenium complex, followed by a [2+2] cyclo-addition reaction between the ruthenium alkylidene and the double bond of the monomer. This results in the formation of a metallacyclobutane intermediate, which can cleave either degeneratively to reform the original components (*Figure 2.4, route a*), or productively to form a new ruthenium alkylidene complex, called the propagating alkylidene (*Figure 2.4, route b*). This productive route is the initiation step.

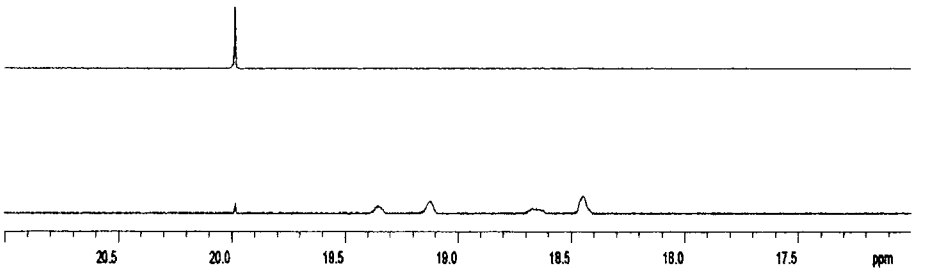


*Figure 2.5. 500 MHz ^1H NMR spectra exhibiting initiation of the ROMP of **2a** mediated by initiator **A** ($CDCl_3$)*

The process of initiation can be monitored using ^1H NMR spectroscopy. The propagating alkylidene proton resonances appear (typically 19.5-18.0 ppm) at the expense of the initiator signal (*Figure 2.5*). The exact chemical shift of the propagating species is dependent on the specific position and nature of the pendant functional groups of the monomer.

2.2.2 Propagation

The insertion of subsequent monomer units into the ruthenium alkylidene bond at the propagating polymer chain-end via [2+2] cyclo-addition reactions is known as propagation. This results in an increase in the length of the polymeric chain and consumption of the monomer (*Figure 2.6*).

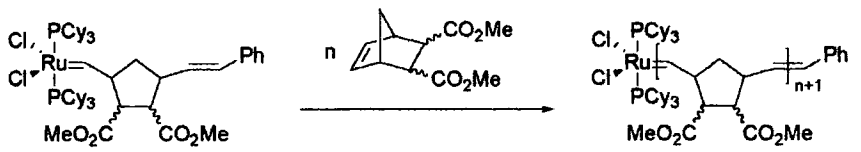


Figure 2.6. The process of propagation when the ROMP of ***2a*** *is mediated by initiator* ***A***

The rate of propagation can be monitored by analysis of the increase in intensity of the resonances of the polymeric olefinic protons (5.6 – 5.1 ppm) at the expense of monomer olefinic protons (6.3 – 6.0 ppm) using ^{1}H NMR spectroscopy (*Figure 2.7*).

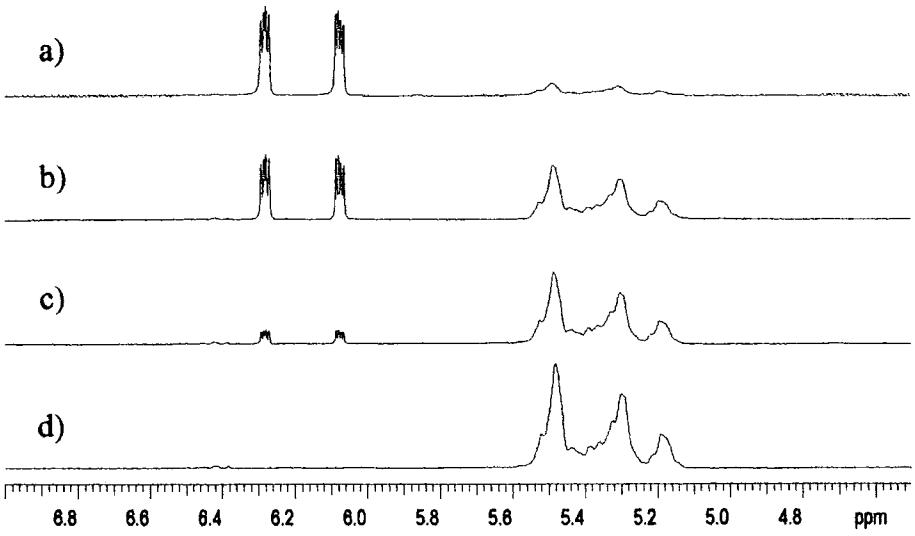


Figure 2.7. The olefinic region of 500 MHz ^{1}H NMR spectra ($CDCl_3$) after a) 0.25, b) 1, c) 2 and d) 6 hours of reaction, when ***2a*** *is subjected to ROMP mediated by initiator* ***A***

2.2.3 Termination

When ROMP is mediated by initiator **A**, the polymerisation reactions are living due to the presence of active propagating alkylidene species in solution once the monomer has been completely consumed.

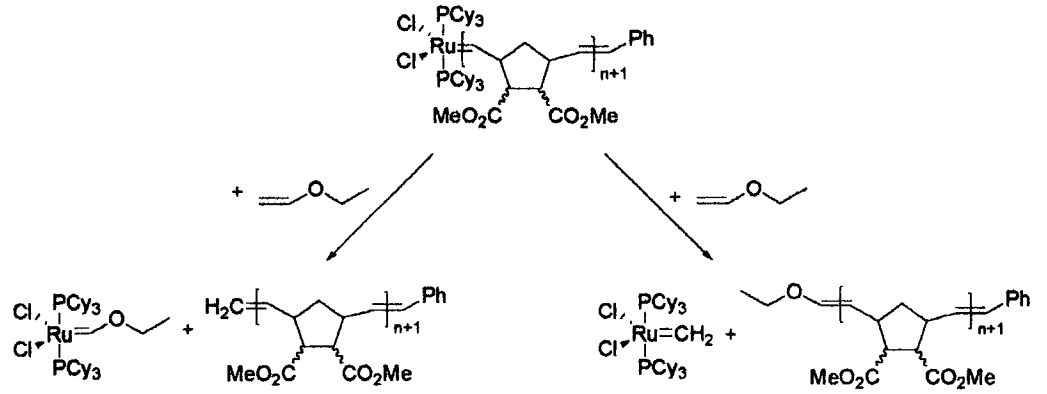


Figure 2.8. The two orientations that ethyl vinyl ether can react with propagating alkylidene species when used to terminate a ROMP reaction

In order to quench a ROMP reaction (i.e. cleaving the polymer from the propagating ruthenium alkylidene species), a terminating agent needs to be introduced. Generally, an acyclic olefin is used to induce the formation of a new ruthenium alkylidene moiety and an end-capped polymer. The standard terminating agent used for ROMP mediated by ruthenium complexes is ethyl vinyl ether. The unsymmetrical nature of ethyl vinyl ether means there are two possible orientations in which it can react with the propagating ruthenium alkylidene species (*Figure 2.8*).

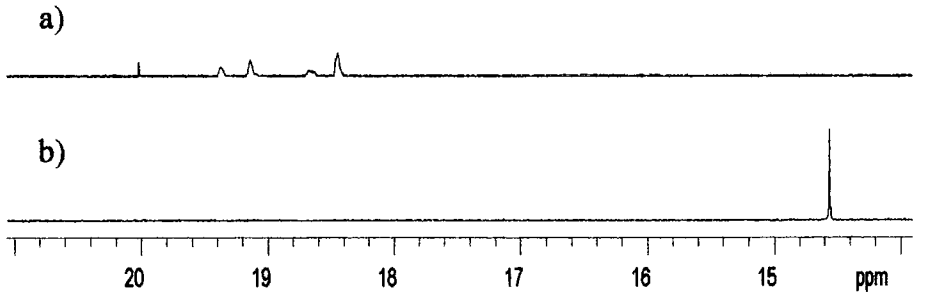


Figure 2.9. 500 MHz ^1H NMR spectra exhibiting termination of the ROMP of ***2a*** *mediated by initiator* ***A*** *using ethyl vinyl ether ($CDCl_3$)*

Ethyl vinyl ether inserts into the propagating ruthenium alkylidene in a manner which results exclusively in the formation of $RuCl_2(PCy_3)_2(=CHOEt)$.[3] This is determined using ^1H NMR spectroscopy by the immediate appearance of a resonance at 14.58 ppm and the disappearance of residual initiator **A** and the propagating alkylidene signals (*Figure 2.9*). If ethyl vinyl ether inserted into the propagating ruthenium alkylidene in the alternative orientation, then an alkylidene resonance for $RuCl_2(PCy_3)_2(=CH_2)$ would be observed at 18.92 ppm.[4,5]

2.3 A ROMP Reaction Exhibiting Regeneration of the Initiator

When initiator **A** was used to mediate the polymerisation of monomer **1**, using a monomer: initiator ratio ($[M]_o/[I]_o$) of 50 in $CDCl_3$, the alkylidene region of the ^1H NMR spectra obtained during the reaction exhibit remarkable behaviour.[1-3] The reaction proceeded rapidly with almost complete consumption of the initiator to form propagating ruthenium alkylidene species, and the monomer was consumed over a period of 1 hour. The propagating species were then seen to convert slowly, but not completely, back to initiator, implying the existence of secondary metathesis reactions. A stack plot of the alkylidene region of ^1H NMR spectra taken at intervals over a 12 hour period showed these extraordinary features, and it clearly exhibits the presence of three distinct signals (*Figure 2.10*).

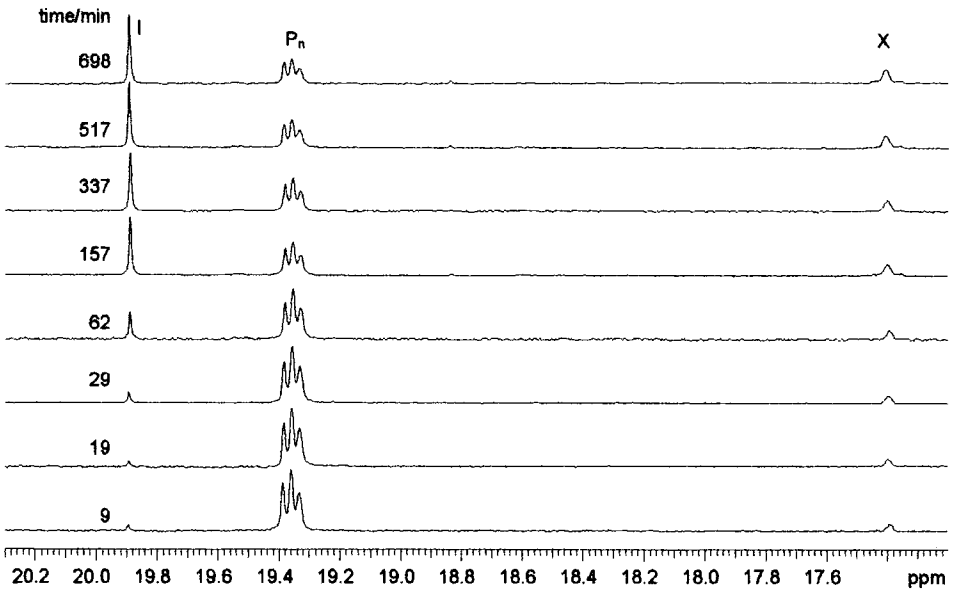


*Figure 2.10. Stack plot of the alkylidene region of ^1H NMR spectra ($CDCl_3$) taken during the first 12 hours of the ROMP of **1** mediated by initiator **A** in $CDCl_3$. $[M]_o/[I]_o=50$, $[I]_o=15$ mM*

The characteristic resonance of the alkylidene proton of initiator **A** is seen at 19.99 ppm, a propagating alkylidene (P_n) has signals at 19.38, 19.36, 19.33 ppm, and a broad species (X) appears at 17.40 ppm. The three propagating signals (P_n) arise due to the sensitivity of the chemical shift to the *cis/trans* isomerism of the adjacent double bond and to the *meso/racemic* isomerism of the adjacent dyad.[3] Since there is no direct relationship between double bond stereochemistry and dyad tacticity, four regular distributions are possible for the monomer units closest to the ruthenium

alkylidene proton (*Figure 2.11*). The appearance of three lines rather than four is attributed to similar *cis/trans* and *meso/racemic* splittings giving rise to overlapping signals.

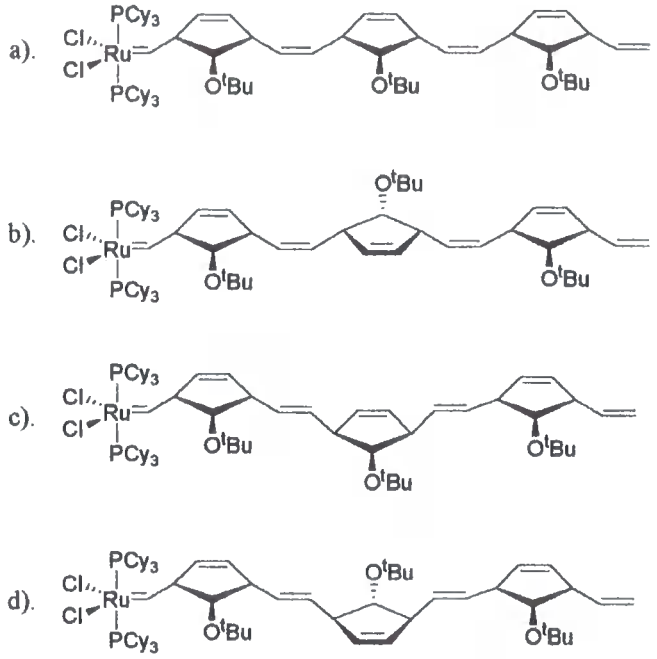


Figure 2.11. Microstructural arrangements of poly(1), a) cis,meso, b) cis,racemic, c) trans,racemic, and d) trans,meso

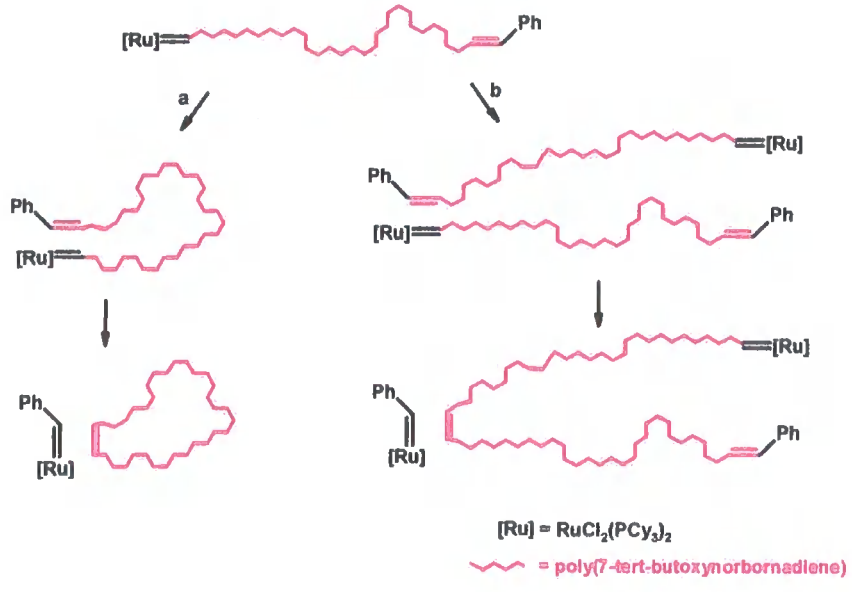


Figure 2.12. Secondary metathesis at the polymer chain-ends by a) intramolecular cyclisation, and b) intermolecular reactions

Over a 24 hour period, the initiator is visibly regenerated at the expense of the propagating species as the reaction proceeds. This can occur by intra- or inter-molecular secondary metathesis reactions at the living chain ends of the propagating polymer chains (*Figure 2.12*). In an intramolecular secondary metathesis reaction, (*Figure 2.12, route a*), the end groups of a discreet propagating chain come into close proximity and react to form a cyclic polymer and regenerate the initiator. Whereas, in intermolecular secondary metathesis reactions (*Figure 2.12, route b*), the end groups from separate propagating polymer chains react, resulting in regeneration of the initiator and a new propagating species, which has the combined molecular weight of the two original propagating chains.

GPC traces of polymer recovered from the system unambiguously demonstrate that one or both of these secondary metathesis reactions must take place (Section 3.2.2).[3] Another consequence of intra- and/or inter-molecular reactions is a decrease in the proportion of end groups of the polymer. This is confirmed by performing the ROMP of monomer **1** mediated by initiator **A** using $[M]_o/[I]_o = 10$, and dividing the solution into two halves. The first half was terminated with ethyl vinyl ether after 40 minutes of reaction, and the second half after 24 hours. Analysis of ^{13}C NMR spectra of the recovered polymers, reveal that the proportion of vinylic end-groups of the first batch was double that of the second batch, supporting the presence of intra- and/or inter-molecular secondary metathesis reactions.[3] The broad alkylidene resonance (X) slowly increases in intensity as the reaction proceeds, and it is extremely stable in solution. The observation of regeneration of the initiator during the ROMP of monomer **1** mediated by initiator **A** is the first of its kind.

2.4 Variations to the System which Exhibits Regeneration of the Initiator

In order to investigate the parameters which govern the process of regeneration of the initiator when monomer **1** is subjected to ROMP mediated by initiator **A**, a number of ROMP systems were studied. In each of the sections described below, a specific parameter of the system was investigated, whilst all other variables remained unchanged.

2.4.1 The Position and Functionality of the Monomer Pendant Groups

A number of bicyclic olefin monomers were subjected to ROMP mediated by initiator **A**, to establish whether regeneration of the initiator was apparent in any of these

systems.[1] The results for the polymerisations of norbornene and the oxygen-containing norbornene derivatives, (*Figure 2.2*, **2-4**), performed under similar conditions to those described for the ROMP of monomer **1** mediated by initiator **A**, are shown in *Table 2.1.*

Table 2.1. ROMP of norbornene and oxygen-containing norbornene derivatives [a]

Monomer	Monomer Consumption	Initiator Consumption
	Hrs	%
2a	14	98
2b	1	95
3a	0.8	69
3b	$< 0.3^b$	91
4	$< 0.3^b$	34

[a] Polymerisations were performed in $CDCl_3$ at ambient temperature and were mediated by initiator **A** using a ratio of $[M]_o/[I]_o$=50. $[I]_o$=15 mM. The reactions were followed by ^{1}H NMR spectroscopy. None of the reactions exhibited regeneration of the initiator. [b] The monomer is completely consumed before the first ^{1}H NMR spectra of reaction mixture is obtained.

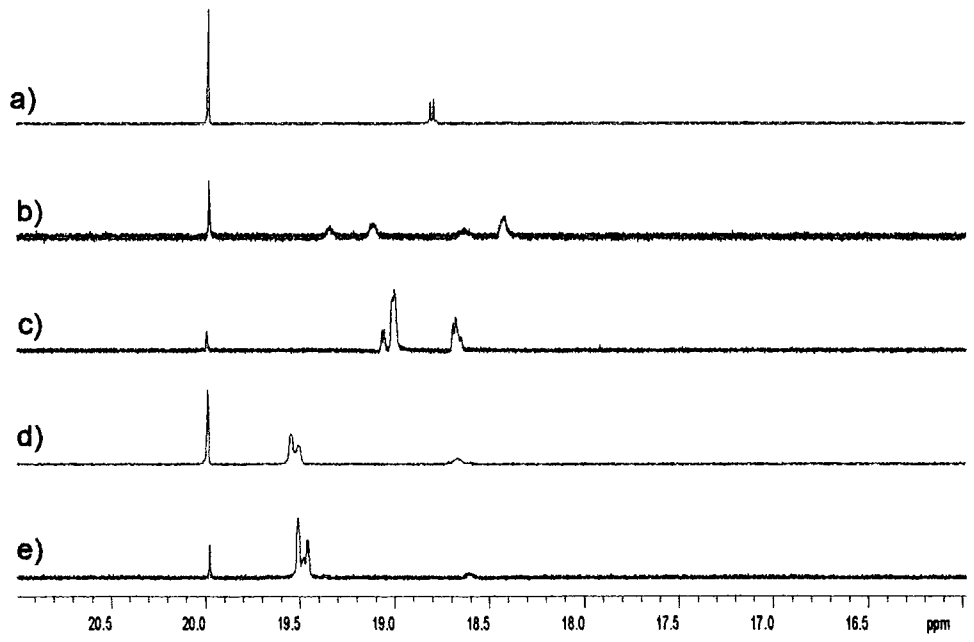


*Figure 2.13. The alkylidene region of 400 MHz ^{1}H NMR spectra ($CDCl_3$) for the ROMP of, a) **4**, b) **2a**, c) **2b**, d) **3a**, and e) **3b** mediated by initiator **A**. $[M]_o/[I]_o$=50, $[I]_o$=15 mM*

The reactions were followed by ^{1}H NMR spectroscopy and, although they behaved differently in terms of the rate of monomer consumption and the amount of initiator consumed, none of the systems exhibited regeneration of the initiator. The alkylidene region (21-16 ppm) of the ^{1}H NMR spectra of these systems are shown in *Figure 2.13*, and stable alkylidene resonances at ~17.5 ppm are not apparent in any of these polymerisation reactions.

2.4.2 The Steric Bulk of the 7-alkoxy Group of the Monomer

The ROMP reactions reported in Sections 2.3 and 2.4.1 suggest that it is the presence of oxygen specifically in the 7-position of the monomer which plays an important role in the process of regeneration of initiator **A**. To investigate this phenomenon, a series of monomers containing alkoxy groups with decreasing steric hindrance in the 7-position were prepared and subjected to ROMP.[1] The ROMP reactions of monomers **5-7** (*Figure 2.2*) mediated by initiator **A** in $CDCl_3$ were monitored by ^{1}H NMR spectroscopy in the same manner as described for monomer **1**.

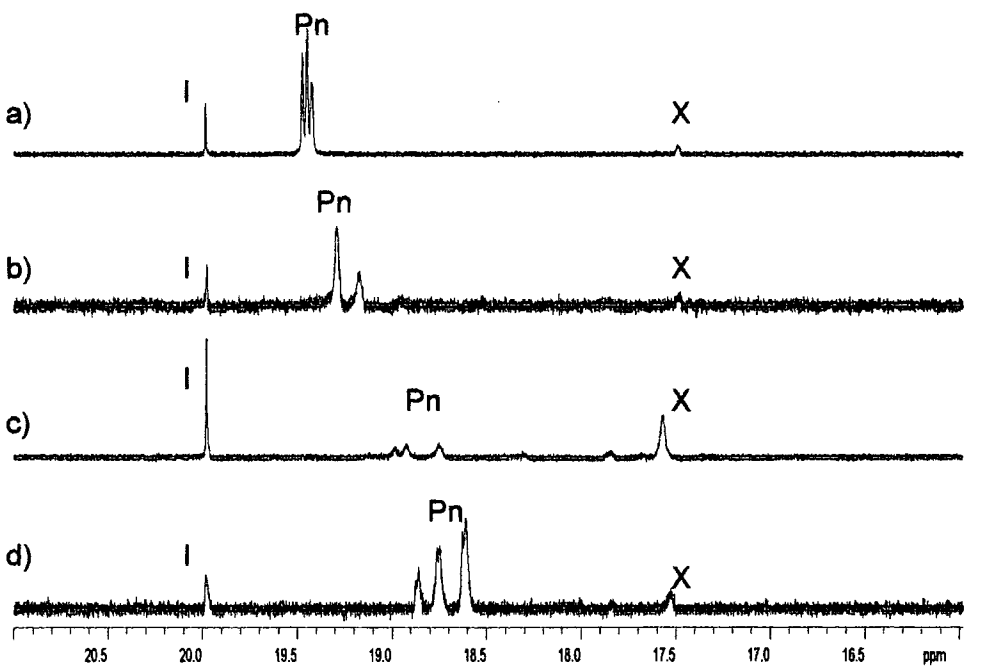


*Figure 2.14. The alkylidene region of 400 MHz ^{1}H NMR spectra ($CDCl_3$) for the ROMP of, a) **1**, b) **5**, c) **6** and d) **7** mediated by initiator **A**. $[M]_o/[I]_o$=50, $[I]_o$=15 mM*

The alkylidene region (21-16 ppm) of the ^{1}H NMR spectra for the ROMP reactions of monomers **1** and **5-7** are shown in *Figure 2.14* and they all exhibit a resonance for the

alkylidene proton of residual initiator **A** (I), the propagating species (P_n) and a stable broad alkylidene species (X) at 19.99, 19.50-18.50, and ~17.5 ppm, respectively.

Regeneration of the initiator was observed in all of these ROMP reactions, *Table 2.2*, and the extent of regeneration is found to increase as the steric bulk of the substituent in the 7-position increases.

*Table 2.2. ROMP of 7-alkoxynorbornadiene monomers (**1** and **5-7**) mediated by initiator **A** [a]*

Monomer	$[M]_o/[I]_o$	Monomer Consumption Hrs	Initial Consumption of Initiator[b] %	Extent of Regeneration[c] %
1	50	1	99	29
1	25	0.5	93	27
1	10	0.25	81	23
5	50	2	98	15
5	25	1	92	18
5	10	0.5	75	13
6	50	5	98	6
6	25	3	92	8
6	10	0.75	71	10
7	50	5.5	97	8
7	25	1	88	3
7	10	0.5	65	1

[a] Polymerisations were performed in $CDCl_3$ at ambient temperature with $[I]_o$=15 mM. The reactions were followed by ^1H NMR spectroscopy. [b] Based on the ^1H NMR spectrum recorded after 15 minutes of reaction. [c] The error associated with the extent of regeneration of the initiator is estimated to be ±5 % of the quoted value.

The process of regeneration is believed to be facilitated by coordination of oxygen in the propagating polymer backbone to the active ruthenium centre.[3] If the chelating oxygen atom happens to be at the chain end of either the same (*Figure 2.15, route a*) or a different propagating species (*Figure 2.15, route b*), then a terminal double bond

is brought into the close proximity of the ruthenium alkylidene. Subsequent secondary metathesis reactions may result in the formation of macrocycles or propagating species of increased molecular weight and regeneration of the initiator. The increased extent of regeneration of the initiator observed when the steric bulk of the 7-alkoxy group is increased, may be attributed to the increased bulk of the alkyl group making the oxygen atom more electron rich, and hence a better electron donating moiety, thus enhancing secondary metathesis reactions at the propagating chain ends.[6]

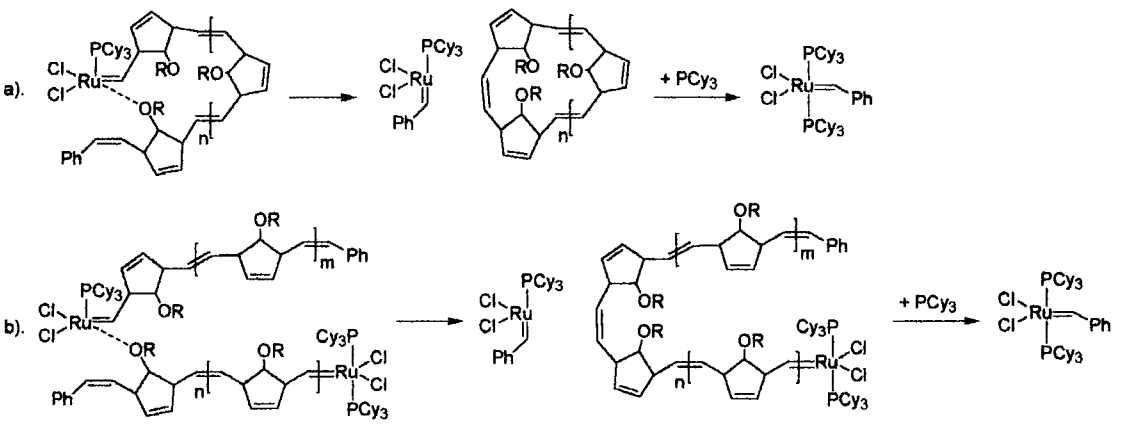


Figure 2.15. Secondary metathesis reactions which result in regeneration of the initiator can be enhanced by a) intra-, or b) inter-molecular chelation of oxygen at the propagating chain end to the ruthenium centre

As shown in *Table 2.2*, polymerisation of the 7-alkoxynorbornadiene monomers mediated by initiator **A** provides information on how the steric bulk of the substituent in the 7-position of the norbornadiene unit affects other aspects of the polymerisation process, such as the rate of monomer consumption and the consumption of initiator at the start of the reaction.[1]

It is well established that a phosphine ligand dissociates from the ruthenium centre in order for initiation and propagation to occur during ROMP mediated by initiator **A**.[7] Dissociation of phosphine makes the ruthenium alkylidene accessible for olefins to undergo the necessary [2+2] cyclo-addition reaction. Once inserted, the monomer unit remains in close proximity to the active ruthenium alkylidene, and its steric bulk has a pronounced influence on the ability of free phosphine to re-associate to the metal centre. It is possible that an increased steric bulk of the 7-alkoxy substituent of the monomer impedes re-association of the PCy_3 ligand, and hence makes the active

site more accessible for the addition of subsequent monomer units. This effect may contribute to faster consumption of the monomer when the steric bulk in the 7-position is increased.

The extent of initiator consumption at the start of the polymerisation decreases when the steric bulk of the 7-alkoxy substituent within the monomer is reduced. This implies that a decrease in the steric bulk of the 7-alkoxy substituent of the monomer enhances the magnitude of the rate of propagation (k_p) relative to the rate of initiation (k_i) during a ROMP reaction mediated by initiator **A**.

2.4.3 The $[M]_o/[I]_o$ Ratio

The effect of the magnitude of $[M]_o/[I]_o$ on the extent of regeneration of the initiator observed during the ROMP of 7-alkoxynorbornadiene monomers, **1** and **5-7**, mediated by initiator **A** has also been studied. *Table 2.2* shows the results of the polymerisations performed on these monomers using $[M]_o/[I]_o$ = 50, 25 and 10.

The process of regeneration observed in these ROMP systems is believed to be in competition with other secondary metathesis reactions such as backbiting, involving internal double bonds along the backbone chains.[3,7] The general trend for the ROMP reactions described in *Table 2.2*, shows that as the $[M]_o/[I]_o$ ratio is reduced, the extent of regeneration of the initiator decreases accordingly. Although the reason for this observation is not fully understood, it implies that a reduction in the length of the propagating polymer chain impedes the occurrence of secondary metathesis reactions at the chain-ends.

2.4.4 Solvent Effects

The effect of the solvent on the process of regeneration of the initiator was studied by monitoring the ROMP of monomer **1** by ^{1}H NMR spectroscopy in $CDCl_3$, CD_2Cl_2 and C_6D_6 (*Table 2.3*).[1] The polarity indices of the solvents according to Allerhand and Schleyer's polarity scale, G, are 106, 100, and 80 respectively.[8] A decrease in the polarity index of the solvent has no significant effect on the amount of initiator **A** initially consumed by monomer **1**, or on the extent of regeneration of the initiator, but the overall kinetics for the polymerisation are retarded (i.e. rate of monomer consumption is reduced and the time period over which regeneration is observed is increased). This trend indicates that an increase in the polarity index of the solvent

increases the rate at which the ROMP of monomer **1** occurs. It also reveals that the media in which the polymerisation of monomer **1** mediated by initiator **A** is performed, plays no role in the regeneration process, and that regeneration occurs solely due to the nature of the monomer and the initiator species present in the system.

Table 2.3. Solvent effects on the ROMP of monomer 1 [a]

Solvent	Regeneration Time Period Days	Monomer Consumption Hrs	Initiator Consumption %	Extent of Regeneration[b] %
$CDCl_3$	1.2	1	99	29
CD_2Cl_2	2.5	3.5	97	29
C_6D_6	3	4.5	100	28

[a] Polymerisations were performed at ambient temperature and were mediated by initiator **A**. $[M]_o/[I]_o$=50. $[I]_o$=15 mM. The reactions were followed by ^{1}H NMR spectroscopy. [b] The error associated with the extent of regeneration of the initiator is estimated to be ±5 % of the quoted value.

2.4.5 ROMP of 5 and/or 6-alkoxy Monomers

As discussed in Section 2.4.2, bicyclic olefin monomers containing alkoxy functionality in the 7-position facilitate the regeneration of initiator **A** during ROMP reactions. In order to establish whether the specific position of the alkoxy functionality within the monomer unit is critical to the process of regeneration of the initiator, *exo*-5-methoxymethylnorbornene (**8**) and *exo,exo*-5,6-bis(methoxymethyl) norbornene (**9**) (*Figure 2.2*) were subjected to ROMP mediated by initiator **A**.[1] The polymerisations were monitored by ^{1}H NMR spectroscopy in the manner described previously. Analysis of the alkylidene region of ^{1}H NMR spectra indicate that these reactions exhibit similar behaviour to the ROMP reactions of monomers **2-4** mediated by initiator **A** described in section 2.4.1 (*Figure 2.16*). Regeneration of the initiator is not observed, and no broad resonances at ~17.5 ppm are apparent. This suggests that it is the specific position of the alkoxy functionality which plays a vital role in the regeneration process and on the formation of the broad resonance at ~17.5 ppm when 7-alkoxynorbornadiene monomers are subjected to ROMP mediated by initiator **A**.

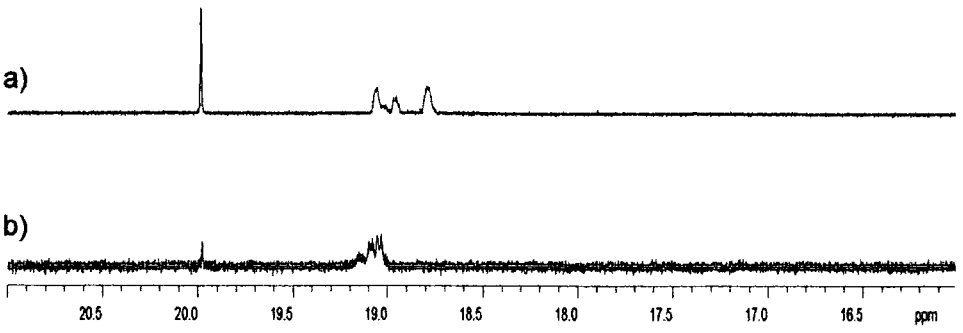


*Figure 2.16. The alkylidene region of 400 MHz ^1H NMR spectra ($CDCl_3$) for the ROMP of, a) **8** and b) **9** mediated by initiator **A**. $[M]_o/[I]_o=50$, $[I]_o=15$ mM*

2.4.6 ROMP of 7-substituted Oxygen-Containing Monomers

It is clear that the presence of alkoxy groups in the 7-position of norbornadiene monomers plays an important role in the process of regeneration when they are subjected to ROMP mediated by initiator **A**.

In order to further investigate the role that oxygen plays, norbornadiene monomers with various oxygen containing functionalities in the 7-position were subjected to ROMP mediated by initiator **A** in $CDCl_3$. The polymerisation of 7-acetoxynorbornadiene (**10**) and 7-hydroxynorbornadiene (**11**) (*Figure 2.2*) were monitored by ^1H NMR spectroscopy and the alkylidene regions of the spectra are shown in *Figure 2.17.*

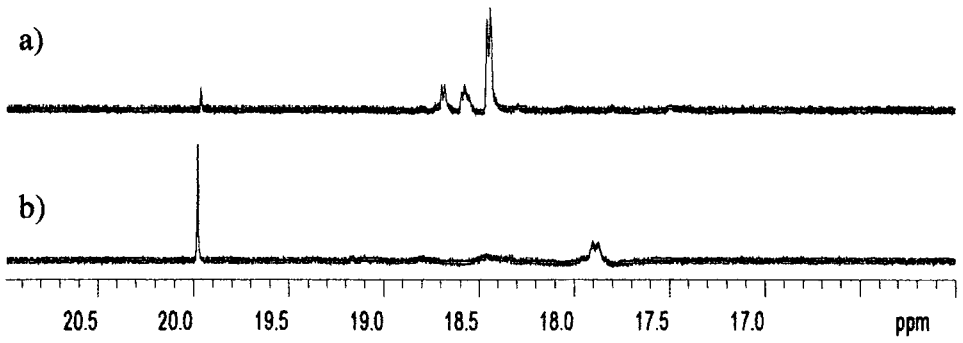


*Figure 2.17. The alkylidene region of 400 MHz ^1H NMR spectra ($CDCl_3$) for the ROMP of a) **10** and b) **11** mediated by initiator **A**. $[M]_o/[I]_o=50$, $[I]_o=15$ mM*

When monomer **10** was subjected to ROMP under these conditions, the alkylidene region of the ^{1}H NMR spectra exhibited proton resonances for residual initiator (19.99 ppm) and propagating species (18.72, 18.61, 18.48 ppm) (*Figure 2.17a*). The monomer was completely consumed after 2 hours of reaction, and 99 % of the initiator was consumed. Regeneration of the initiator was observed at the expense of the propagating species, and reached a maximum value (6 %), after 6 hours of reaction. Interestingly, unlike the ROMP of 7-alkoxynorbornadiene monomers, no alkylidene resonances were observed at ~17.5 ppm during the reaction. This indicates that the specific environment of the oxygen functionality must affect its ability to chelate to the ruthenium centre.

When the ROMP of monomer **11** was mediated by initiator **A**, after 6 hours of reaction, a precipitate formed and consequently no more ^{1}H NMR spectra were obtained. Precipitation was believed to occur due to the increased local concentration of OH groups, as the propagating poly(**11**) chains grew in length, increasing the extent of hydrogen bonding within the polymer backbone. Hence increasing its hydrophilic nature and rendering it insoluble in organic media. The alkylidene region of the ^{1}H NMR spectra taken during the first 6 hours of reaction exhibit a signal for the residual initiator (19.99 ppm) and many broad signals (19.2-17.8 ppm) for the propagating alkylidene species (*Figure 2.17b*). Initially, 50 % of the initiator was consumed. Consumption of monomer was very slow, and at the point were precipitation occured only 27 % had been polymerised. No regeneration of the initiator was observed during the reaction and no stable alkylidene species appeared at ~17.5 ppm. However, no clear conclusions can be made on the ROMP of this monomer, due to precipitation occurring before the polymerisation reached completion.

2.4.7 The Nature of the Ruthenium Alkylidene Complex

So far in this chapter, the effect that the nature of the monomer has on the process of regeneration of the initiator has been explored in detail. Regeneration has been observed during the polymerisation of bicyclic olefin monomers which contain oxygen in the 7-position mediated by initiator **A**. In this section, the role that the ruthenium complex plays in the regeneration process is explored, and particular attention is paid to the chemistry of the ligands. Grubbs type 1st, 2nd and 3rd generation ruthenium complexes (*Figure 2.1*, **A-E**) were employed to perform the

ROMP of monomer **1**. The results of these polymerisations are shown in *Table 2.4*, and the alkylidene regions of ^{1}H NMR spectra taken of the systems are shown in *Figure 2.18*.

*Table 2.4. The effect of the nature of the ruthenium initiator (**A-E**) on the ROMP of monomers **1** and **2a** [a]*

Initiator	Monomer	Monomer consumption / hrs	Initiator consumption / %	M_n [e,f]	PDI
A	**1**	0.5	90	11,004	1.12
B	**1**	- [b]	46	-	-
C	**1**	< 0.25 [d]	< 1	22,542	1.78
D	**1**	0.5	< 1	32,732	2.86
E	**1**	< 0.25 [d]	100	3,826	1.12
A	**2a**	3	93	2,528	1.15
B	**2a**	- [c]	75	-	-
C	**2a**	< 0.25 [d]	< 1	93.745	1.54
D	**2a**	1	2	111,862	1.63
E	**2a**	< 0.25 [d]	100	3,011	1.06

[a] Polymerisations were performed in $CDCl_3$ at ambient temperature with $[M]_o/[I]_o$=20, $[M]_o$=0.35 M. The reactions were followed by ^{1}H NMR spectroscopy. [b] < 10 % of monomer consumed before all alkylidene species decompose. [c] < 5 % of monomer consumed before all alkylidene species decompose. [d] The monomer is completely consumed before the first ^{1}H NMR spectra of reaction mixture is obtained. [e] The quoted values are relative to polystyrene standards. [f] Predicted M_n for poly(**1**) and poly(**2a**) are 3,300 and 4,200 respectively.

Regeneration of the initiator was only observed in the system mediated by initiator **A**. The other ruthenium complexes (**B-E**) displayed a variety of behaviours when employed for ROMP. In order to confirm that this behaviour was not solely due the nature of monomer **1**, the ROMP of monomer **2a**, a bench-mark monomer, was also performed with each of the ruthenium complexes. The alkylidene regions of ^{1}H NMR spectra for these polymerisations are shown in *Figure 2.19*. In all of the systems, the polymerisation was terminated with ethyl vinyl ether upon complete consumption of the monomer. The polymer was recovered and analysed by GPC (*Table 2.4*).

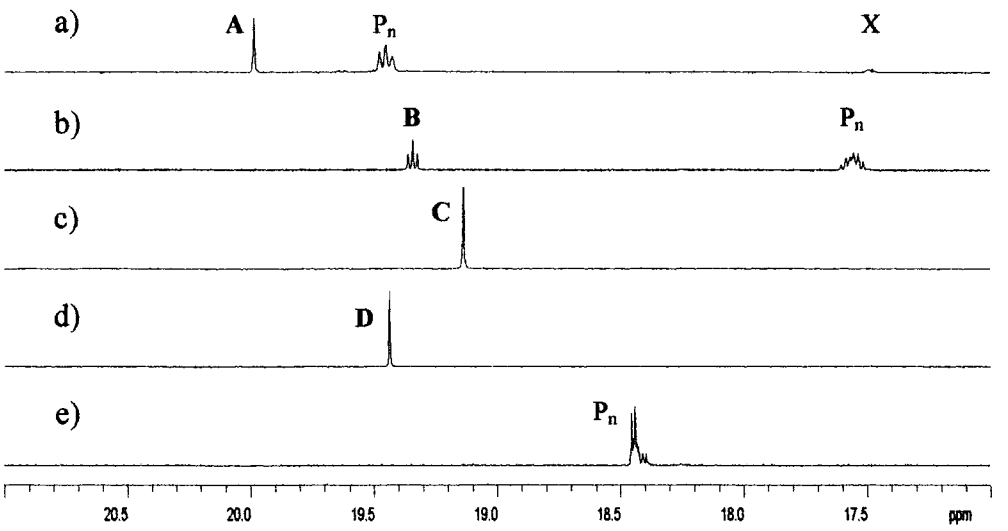


Figure 2.18. The alkylidene region of 500 MHz ^1H NMR spectra ($CDCl_3$) for the ROMP of ***1*** *mediated by initiators a)* ***A****, b)* ***B****, c)* ***C****, d)* ***D*** *and e)* ***E****. $[M]_o/[I]_o$=20, $[M]_o$=0.35 M*

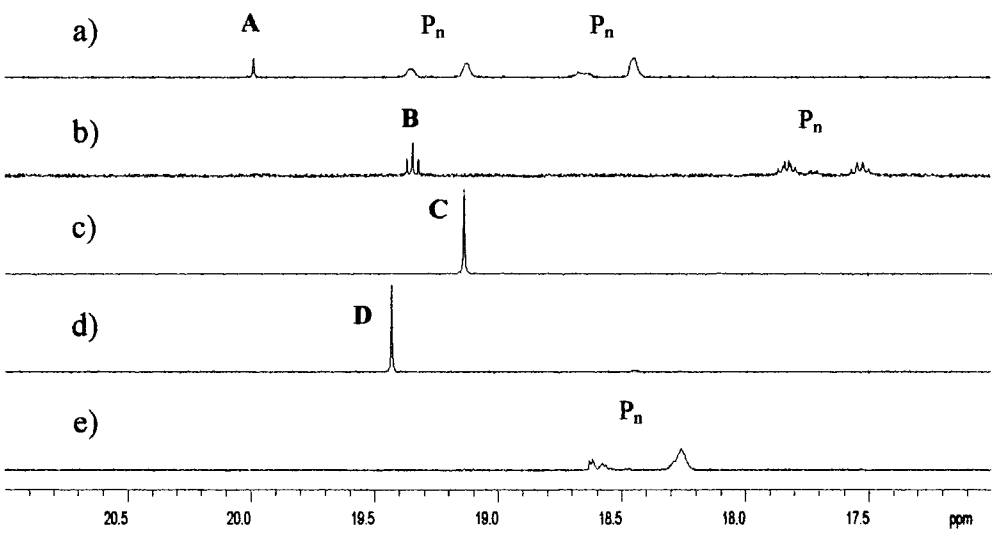


Figure 2.19. The alkylidene region of 500 MHz ^1H NMR spectra ($CDCl_3$) for the ROMP of ***2a*** *mediated by initiators a)* ***A****, b)* ***B****, c)* ***C****, d)* ***D*** *and e)* ***E****. $[M]_o/[I]_o$=20, $[M]_o$=0.35 M*

When $RuCl_2(PPh_3)_2$(=CHPh) (**B**) was used to mediate the ROMP of the two oxygen containing monomers (**1** and **2a**), the systems were found to be inherently unstable and the polymerisation proceeded very slowly. The alkylidene species diminished in

intensity as the reaction proceeded, and in both cases, by the time they had completely decomposed, less than 10 % of the monomer had been consumed. Consequently no polymer was recovered from the reaction. These two systems highlight the sensitive nature of ruthenium alkylidene species. It is apparent that a subtle change to the basicity and steric bulk of the phosphine ligand impacts massively on the stability and metathesis activity of the ruthenium alkylidene complex.

Grubbs 2nd generation ruthenium complexes are highly active for olefin metathesis, and this is attributed to the highly basic nature of the substituted *N*-mesityl imidazole ligands. The presence of these electron rich ligands promotes the loss of PCy_3 from the metal centre to generate the active site, and enhances the initiators activity towards olefins. When $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$ (**C**) was used to mediate the ROMP of monomers **1** and **2a**, the monomers were consumed within 15 minutes, with less than 1 % of the initiator being consumed. This is indicative of systems in which k_p is considerably larger than k_i, and this is reflected in the high M_n values of the resulting polymers. Saturated imidazole ligands ($IMesH_2$) are more basic than their unsaturated counterparts (IMes), and so the catalytic activity of $RuCl_2(PCy_3)(IMes)(=CHPh)$ (**D**) would be expected to be lower than initiator **C**. This was found to be the case, and the polymerisation of monomers **1** and **2a** were found to proceed more slowly when mediated by initiator **D**. However, the ratios of k_p/k_i were still found to be extremely high, and only a fraction of the initiator was consumed. This resulted in the polymerisations being uncontrolled, and the resultant polymers having high molecular weights and relatively broad polydispersites. Although 2nd generation ruthenium complexes are highly active for olefin metathesis, they are not an appropriate choice for mediating the ROMP of bicyclic olefin monomers of this kind.

The 3rd generation ruthenium initiator, $RuCl_2(3\text{-}BrPyr)_2(IMesH_2)(=CHPh)$ (**E**), was found to be highly active for the ROMP of monomers **1** and **2a**, and in both systems the monomer was consumed in less than 15 minutes of reaction. Initiator **E** is a far better ROMP catalyst than the 2nd generation ruthenium complexes (**C** and **D**), and this is attributed to its high activity not compromising its high value of k_i/k_p. This is reflected by the initiator being completely consumed during the polymerisations, and the recovered polymers having very narrow polydispersites and low molecular weights.

2.5 Properties and ROMP Activity of Species X

The parameters which govern the process of regeneration of the initiator have been investigated in detail. Species X, which appears in ^{1}H NMR spectra during the polymerisation of 7-alkoxynorbornadiene monomers is now considered. The presence of species X during the ROMP of 7-alkoxynorbornadiene monomers is clearly shown in *Figure 2.14*. In all cases species X is stable and long-lived.

When 7-methoxynorbornadiene (**7**) was subjected to ROMP mediated by initiator **A**, species X was still present in solution after 1 month of reaction, and was the only alkylidene species observed by ^{1}H NMR spectroscopy (*Figure 2.20*). The absence of the initiator and propagating species after this time is consistent with the known rates of decomposition of ruthenium alkylidene species,[5] and it is remarkable that species X remained in solution. A second batch of monomer **7** (18 equiv. added after 33 days of reaction), was consumed very slowly (20 days), and during this time the appearance of the alkylidene region remained unchanged. This observation implies that X is able to perform ROMP on strained cyclic olefins.

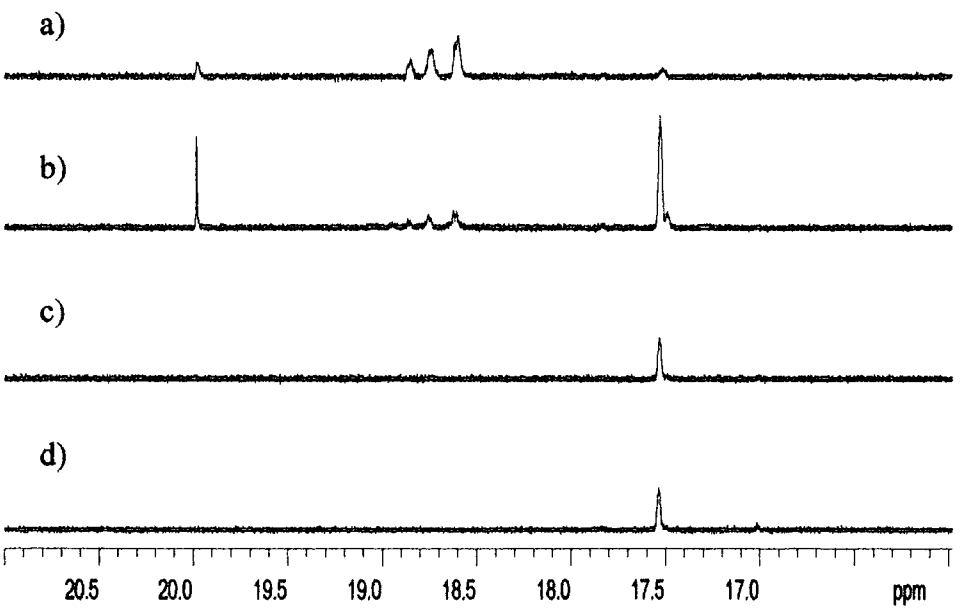


Figure 2.20. The alkylidene region of 400 MHz ^{1}H NMR spectra ($CDCl_3$) for the ROMP of 7 mediated by initiator A after a) 15 minutes, b) 48 hours, c) 22 days of reaction. d) after 33 days of reaction plus 18 equiv. of 7. $[M]_o/[I]_o$=50, $[I]_o$=15 mM

Species X is believed to be a mono(phosphine) propagating species in which oxygen from the propagating polymer backbone chelates to the ruthenium centre. An oxygen

atom emanating from the polymer chain-end and chelating to the ruthenium centre would bring a terminal double bond into the close proximity of the active propagating site and hence facilitate the regeneration process. This can happen either intra- or inter-molecularly and is discussed in further detail in Chapter 3.

2.6 Summary

When 7-alkoxynorbornadiene monomers are subjected to ROMP mediated by initiator **A**, the initiator is consumed and then partially regenerated at the expense of the propagating alkylidene species. This is believed to occur by either intra- or inter-molecular secondary metathesis reactions at the chain ends of the living propagating polymers.

The parameters that govern the process of regeneration of the initiator have been studied. The ROMP of bicyclic olefin monomers containing oxygen functionality in positions other than the bridgehead carbon, results in no regeneration of the initiator. Similarly, subtle variations to the chemistry of the ligands of the initiator result in no regeneration being observed. Changes to the polarity of the solvent in which the polymerisation was performed was found to have no significant effect on the extent of regeneration of the initiator, but as the polarity of the solvent was reduced the overall kinetics for the polymerisation were retarded.

The extent of regeneration of the initiator observed when 7-alkoxynorbornadiene monomers were subjected to ROMP mediated by initiator **A**, was found to decrease as the steric bulk of the substituent in the 7-position decreased. A decrease in the ratio of $[M]_o/[I]_o$ was also found to impede the extent of regeneration of the initiator that was observed.

The results from this chapter suggest that the specific position of the alkoxy functionality of the monomer, coupled with the electronic properties of ligands contained within the well-defined ruthenium complex, play a vital role in the process of regeneration of the initiator when 7-alkoxynorbornadiene monomers are subjected to ROMP mediated by initiator **A**.

During the ROMP of 7-alkoxynorbornadiene monomers, a small amount of another alkylidene species (X), giving rise to a broad signal at ~17.5 ppm, was formed. This

species was found to be extremely stable in solution, and was active for olefin metathesis. The chemical structure of species X and the mechanism by which it performs ROMP is studied in further detail in chapter 4.

2.7 References

1. D. M. Haigh, A. M. Kenwright, E. Khosravi, *Tetrahedron* **2004**, *60*, 7217.
2. K. J. Ivin, A. M. Kenwright, E. Khosravi, *Chemical Communications* **1999**, 1209.
3. K. J. Ivin, A. M. Kenwright, E. Khosravi, J. G. Hamilton, *Macromolecular Chemistry and Physics* **2001**, *202*, 3624.
4. P. Schwab, R. H. Grubbs, J. W. Ziller, *Journal of the American Chemical Society* **1996**, *118*, 100.
5. M. Ulman, R. H. Grubbs, *Journal of Organic Chemistry* **1999**, *64*, 7202.
6. McMurry, *Organic Chemistry: 4th Edition*, Brooks/Cole, **1998**.
7. C. W. Bielawski, R. H. Grubbs, *Macromolecules* **2001**, *34*, 8838.
8. A. Allerhand, P. v. R. Schleyer, *Journal of the American Chemical Society* **1963**, *85*, 371.

Chapter 3

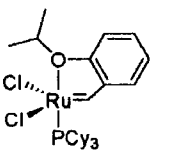
A Study on the Ligand Exchange and ROMP Activity of a Stable Ruthenium Alkylidene Complex Containing Internal Oxygen-Chelation

3.1 Introduction

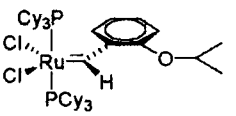
The previous chapter reports the phenomenon of regeneration of the initiator when 7-alkoxynorbornadiene monomers (*Figure 2.2*, **1, 5-7**) are subjected to ROMP mediated by $RuCl_2(PCy_3)_2(=CHPh)$ (*Figure 2.1*, **A**). In these systems, the alkylidene proton resonances were observed by ^1H NMR at ~17.5 ppm, and were found to be very stable in solution. These resonances are believed to arise from mono(phosphine) ruthenium alkylidene propagating species in which oxygen contained within the propagating polymer backbone chelates to the metal-centre. It is possible that chelation of an oxygen atom from the propagating polymer chain end to the ruthenium centre (either intra- or intermolecularly), brings terminal double bonds into the close proximity of the ruthenium alkylidene, and hence encourages secondary metathesis reactions which result in regeneration of the initiator (*Figure 2.15*).

This chapter introduces $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)$ (*Figure 3.1*, **F**), a stable ruthenium alkylidene complex containing internal oxygen chelation to the ruthenium centre. The ligand exchange and ROMP activity of this complex is studied, and analogies are drawn between its structure and the structure of the mono(phosphine) alkylidene species observed when initiator **A** mediates the ROMP of 7-alkoxynorbornadiene monomers.

The chemical structure of the ruthenium alkylidene complexes and the bicyclic monomers discussed in this chapter are depicted in *Figures 2.1*, *2.2* and *3.1*.



F



G

12a: R = $CH_2C(CH_3)_3$
12b: R = CH_2CH_3
12c: R = CH_3

*Figure 3.1. $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)$ [**F**], $RuCl_2(PCy_3)_2(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)$ [**G**], 7-neopentylnorbornadiene [**12a**], 7-ethylnorbornadiene [**12b**], 7-methylnorbornadiene [**12c**]*

3.2 Ruthenium Complex Containing Internal Ruthenium-Oxygen Chelation

Hoveyda *et al.*, recently reported the synthesis of the ruthenium complex **F**.[1] It is structurally similar to initiator **A**, except that a PCy_3 ligand has been replaced by an oxygen atom which emanates from the *iso*-propoxy functionality of the benzylidene moiety. The alkylidene proton resonance of initiator **F** appears as a doublet (J_{PH} = 4.4 Hz) by ^1H NMR spectroscopy, due to coupling with the phosphorous nucleus of the PCy_3 ligand (*Figure 3.2a*).

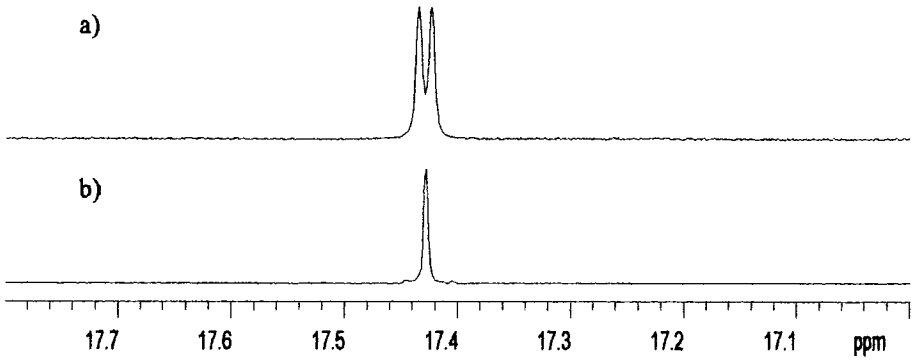


*Figure 3.2. The characteristic alkylidene proton resonance of initiator **F** observed by a) $^1H - ^{31}P$ coupling and b) $^1H\{^{31}P\}$ NMR spectroscopy (500 MHz, $CDCl_3$)*

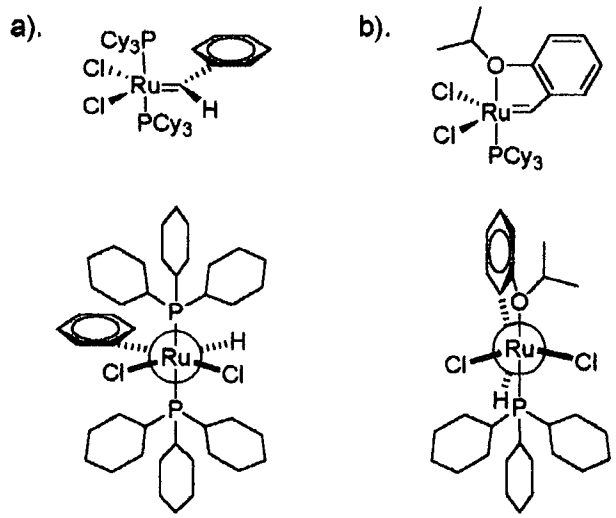


*Figure 3.3. Representation of the structures of a) initiator **A** and b) initiator **F***

This coupling is not seen in the case of initiator **A** (P-Ru-C_α-H_α dihedral angle = 90°), and it arises due to the formation of the five-membered ring coinciding with a 90° rotation about the carbon-metal double bond, thus moving the alkylidene proton into

the same plane as the phosphorous nucleus (*Figure 3.3*).[1] In the ^{1}H $\{^{31}P\}$ NMR spectrum of initiator **F**, the alkylidene proton resonance appears as a singlet, confirming the presence of phosphorous-proton coupling (*Figure 3.2b*).

3.2.1 Characteristics of Initiator F

Initiator **F** is of significant interest to the work covered in this thesis, due to the resonance of its alkylidene proton appearing at 17.44 ppm in ^{1}H NMR spectra. The relatively low frequency of chemical shift for the alkylidene proton (*cf.* initiator **A** at 19.99 ppm) is attributed to chelation of an ethereal oxygen to the ruthenium centre, resulting in the formation of a 5-membered ring. Its chemical shift by ^{1}H NMR spectra is comparable to those of the stable alkylidene resonances (species X) seen when initiator **A** is used to mediate the ROMP of monomer **1**. The fact that both initiator **F** and species X are stable in solution over extended periods of time is also worthy of comment. The analogous structures and enhanced stability prompted the study of ligand exchange and ROMP reactions involving initiator **F**.

3.2.2 The Stability of Initiator F Relative to Initiator A

The enhanced stability of initiator **F** relative to initiator **A** became apparent when a sample of each was dissolved in dry degassed $CDCl_3$ and monitored by ^{1}H NMR spectroscopy (*Figure 3.4*). The intensity of the alkylidene proton resonance of initiator **A** diminished by 20 % after 24 hours in solution, and the remaining 80 % steadily decomposed over a 35 day period. The pathway to decomposition of initiator **A** is believed to occur by dissociation of a phosphine ligand followed by the coupling of two mono(phosphine) species to form unstable bimetallic centres (Section 1.4.4.4).[2] The decrease in the rate of decomposition of initiator **A** is attributed to the stabilising effect of free PCy_3 which is generated as a by-product from decomposed complex. Over the same 35 day period, the intensity of the alkylidene proton resonance of initiator **F** was found to diminish by less than 5 %.

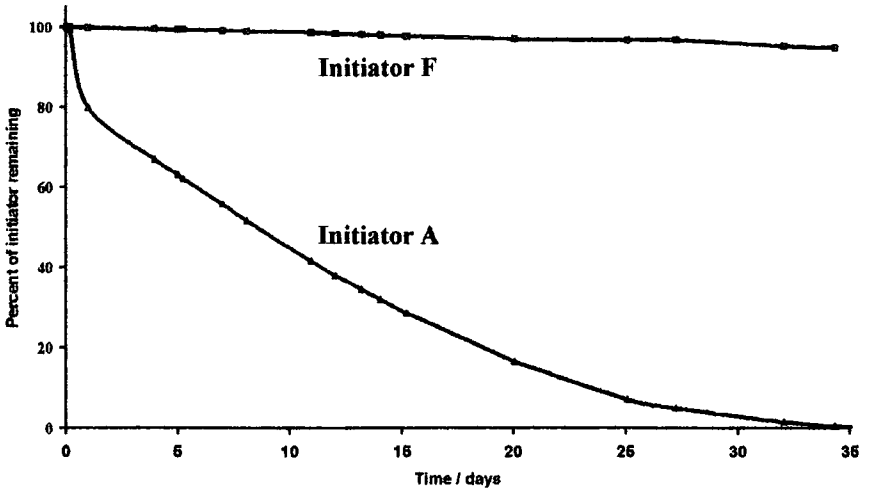


*Figure 3.4. The disappearance of the alkylidene proton resonances of initiator **A** and initiator **F**, when dissolved in $CDCl_3$ and followed by ^1H NMR spectroscopy*

The marked difference in stability of the two ruthenium complexes is attributed to the presence of internal ruthenium-oxygen chelation in initiator **F**.[1] This is consistent with the observation that propagating species X are more stable than the bis(phosphine) propagating species that arise when 7-alkylnorbornadiene monomers are subjected to ROMP mediated by initiator **A** (Section 4.2.5).[3]

3.2.3 Induced Formation of a Substituted Benzylidene Analogue of Initiator A

In order to assess whether the chelating oxygen atom of initiator **F** could be displaced to give rise to a substituted bis(phosphine) benzylidene analogue of initiator **A**, 1 and 5 equivalents of PCy_3 were added to separate portions of this complex dissolved in $CDCl_3$. In both systems, the ^1H NMR spectra (*Figure 3.5a*) exhibited resonances at 17.44 ppm for the alkylidene proton of initiator **F**. Also resonances were observed at 20.55 ppm which were assigned to $RuCl_2(PCy_3)_2(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)$ (*Figure 3.1*, **G**). The ratio of the signals at 17.44 and 20.55 ppm when 1 and 5 equivalents of PCy_3 were added was 85:15 and 50:50, respectively. The ^{31}P NMR spectra of the two solutions exhibit three major signals at 59.8, 36.4 and 12.2 ppm which correspond to initiator **F**, initiator **G** and free PCy_3, respectively (*Figure 3.5b*). The small resonance at 50.9 ppm is an impurity from the added PCy_3.

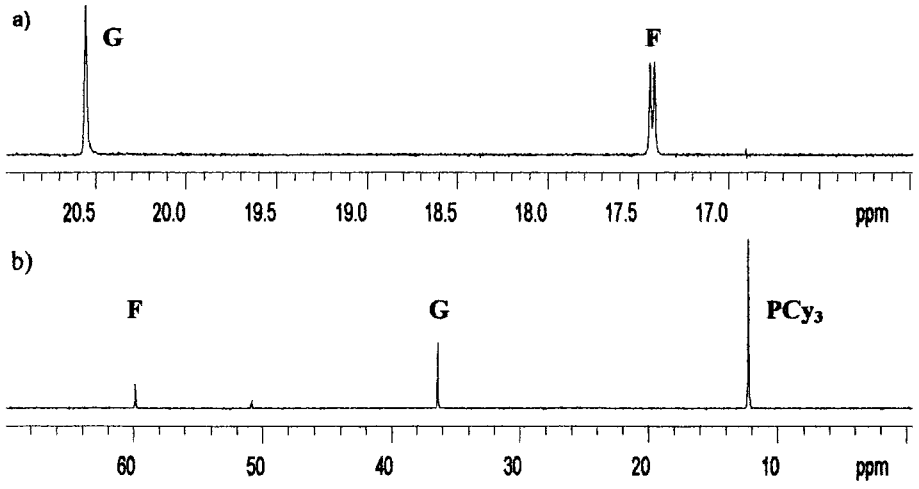


Figure 3.5. a) The alkylidene region of 500 MHz ^{1}H NMR spectra ($CDCl_3$) and b) 202 MHz ^{31}P NMR spectra, when 5 equivalents of PCy_3 are added to initiator **F**

Initiator **G** forms by displacement of the chelating *iso*-propoxy oxygen atom of initiator **F** by PCy_3 which gives rise to an *iso*-propoxy-substituted benzylidene analogue of initiator **A** (*Figure 3.6*). The resonance due to the alkylidene proton of initiator **G** appears as a singlet due to a 90° rotation about the carbon-metal double bond when the *iso*-propoxy ethereal oxygen is displaced, thus moving the alkylidene proton out of the same plane as the phosphorous nucleus (*cf.* Initiator **A**, *Figure 3.3a*).

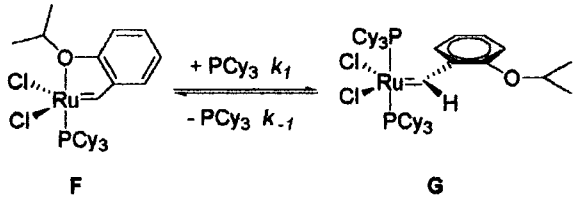


Figure 3.6. The equilibrium that exists between initiator **F** *and initiator* **G** *in the presence of PCy_3*

3.3 Evaluation of Initiator F for Mediating ROMP

The first use of complex **F** as an initiator for ROMP was reported by Hoveyda *et. al.* when it was employed to polymerise cyclo-octadiene.[1] It was reported that the alkylidene protons of propagating species were not detectable by NMR spectroscopy during this reaction, and this was attributed to their high activity and instability on the NMR time-scale. Subsequent publications report that propagating alkylidene proton resonances are detectable when initiator **F** is used to mediate the ROMP of other

cyclic monomers.[4-8] Interestingly, in all of the systems where propagating species are observable, the monomers being subjected to ROMP contain oxygen. In this section, the ROMP capability of initiator **F** is explored, and structural determination of the propagating species that arise in the ^{1}H NMR spectra are investigated.

3.3.1 ROMP of Norbornadiene Derivatives

In order to evaluate the ROMP capability of initiator **F**, it was used to mediate the polymerisation of monomer **1** and 7-ethylnorbornadiene (**12b**). The polymerisations were terminated by addition of ethyl vinyl ether once the monomer had been completely consumed, and the polymer was subsequently recovered. For comparison, initiator **A** was used to mediate the ROMP of the same monomers under analogous conditions. The results are detailed in *Table 3.1.*

*Table 3.1. Results for the ROMP of **1** and **12b** mediated by initiators **A** and **F** [a]*

Monomer	Initiator	Monomer consumption / hrs	M_n [c,d]	PDI
1	**A**	1	5,648	1.79
1	**F**	2	16,925	2.67
12b	**A**	<0.25[b]	-	-
12b	**F**	<0.3[b]	-	-

[a] $[I]_o$ for initiator **A** and initiator **F** is 15 and 20 mM, respectively. $[M]_o/[I]_o$=50. polymerisations performed in $CDCl_3$ at ambient temperature. The reactions were followed by ^{1}H NMR spectroscopy. [b] the monomer is consumed before the first ^{1}H NMR spectrum is obtained. [c] The quoted values are relative to polystyrene standards. [d] Predicted M_n for poly(**1**) and poly(**12b**) are 8,200 and 6,000, respectively.

The first step of the mechanism of ROMP reactions mediated by initiator **A** involves dissociation of a phosphine ligand in order to make the ruthenium alkylidene bond accessible for olefins to undergo the necessary [2+2] cyclo-addition reaction.[6,9] The proposed mechanism for the initiation step of olefin metathesis reactions performed by initiator **F** implies that the *iso*-propoxystyrenyl ligand, and not PCy_3, dissociates from the ruthenium centre.[1] Therefore, it is expected that the rate of initiation for complex **F** will be slower in comparison to that of initiator **A**, due to less facile dissociation of the smaller *iso*-propyl aryl ether ligand (relative to PCy_3) from the sterically congested metal centre. This is reflected in the fact that < 5% of initiator **F** was consumed when used to mediate the ROMP of monomers **1** and **12b**.

3.3.1.1 Identity of Propagating Species that arise during ROMP

When monomer **12b** was subjected to ROMP mediated by initiator **F**, no propagating species were observed and the alkylidene region of the ^{1}H NMR spectrum simply showed a resonance for the alkylidene proton of residual initiator **F** (*Figure 3.7a*). The polymerisation proceeded very quickly and the monomer had been completely consumed by the time the first ^{1}H NMR spectrum was obtained (< 20 minutes).

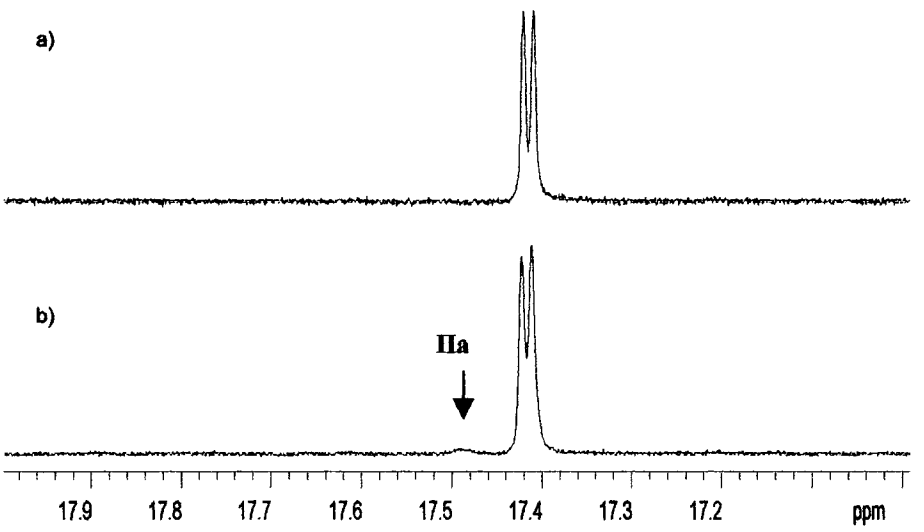


*Figure 3.7. The alkylidene region of 500 MHz ^{1}H NMR spectra ($CDCl_3$) when monomers a) **12b** and b) **1** are subjected to ROMP mediated by initiator **F**. $[M]_o/[I]_o$=50, $[I]_o$=20 mM*

The ROMP reaction of monomer **1** mediated by initiator **F** proceeded much more slowly than that of monomer **12b**, and the monomer was consumed over a 2 hour period. The alkylidene region of the ^{1}H NMR spectrum exhibited a major peak for the proton of residual initiator **F** and a small broad signal could be seen at 17.49 ppm (*Figure 3.7b*, **IIa**). The intensity of this resonance was about 1/40 of that of residual initiator **F** and is tentatively attributed to the alkylidene proton of the propagating species **IIa** in which oxygen from the propagating poly(1) backbone chelates to the ruthenium centre (*Figure 3.8b*). The species is also visible by ^{31}P NMR spectroscopy at 56.3 ppm (*Figure 3.9b*).

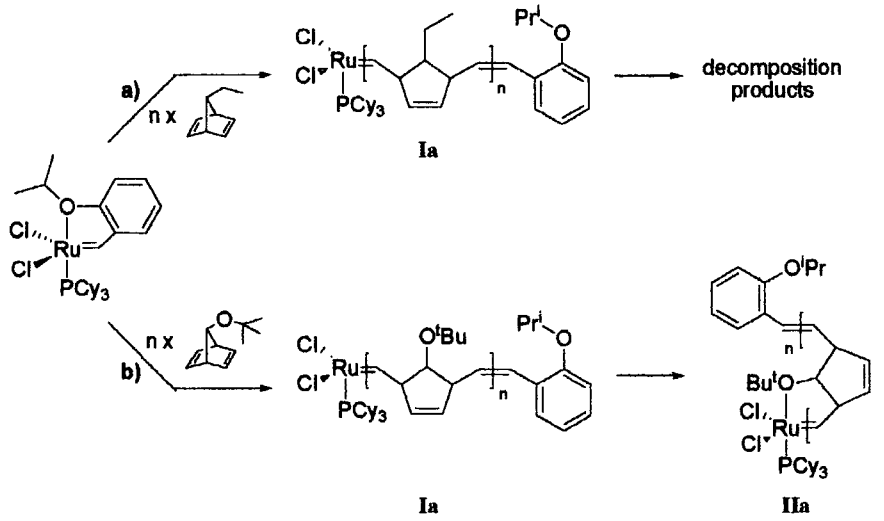


*Figure 3.8. Representation of the propagating alkylidene species that may form during the ROMP of a) **12b** and b) **1** mediated by initiator **F***

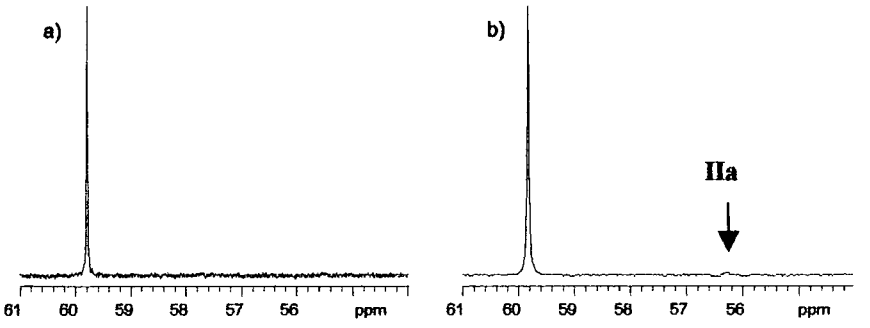


*Figure 3.9. The 202 MHz ^{31}P NMR spectra ($CDCl_3$) when the ROMP of a) **12b** and b) **1** are mediated by initiator **F**. $[M]_o/[I]_o=50$*

It is possible that the presence of species **IIa** reduces the rate of consumption of monomer **1** relative to the ROMP of monomer **12b** mediated by the same initiator. Chelation of oxygen to the ruthenium centre inhibits the association of monomer into the active propagating ruthenium alkylidene. The mono(phosphine) oxygen-chelated alkylidene species **IIa** is analogous to that of species X which can also be observed by ^1H and ^{31}P NMR spectroscopy when initiator **A** is used to mediate the ROMP of monomer **1**. Further evidence for chelation of oxygen to the ruthenium centre in species X is described in Section 4.4.1.

Unlike initiator **A**, when the polymerisation of monomer **1** was mediated by initiator **F** the alkylidene proton resonances for bis(phosphine) propagating alkylidene species (19.36 ppm, t) were not observed. This was attributed to the absence of free PCy_3 in

the system. In an attempt to induce the appearance of the bis(phosphine) propagating signals, 5 equivalents of PCy_3 were added once the monomer had been consumed. A resonance for the alkylidene proton of initiator **G** was observed at 20.55 ppm. However, alkylidene proton resonances for the bis(phosphine) propagating species were undetectable by ^1H or ^{31}P NMR spectroscopy. This may be due to a low concentration of this type of propagating species in the system, since less than 5% of the initiator was consumed.

No propagating alkylidene resonances were observed during the ROMP of monomer **12b** mediated by initiator **F** by either ^1H or ^{31}P NMR spectroscopy due to the absence of both oxygen in the polymer backbone and free PCy_3 to chelate to the ruthenium centre (*Figures 3.7a, 3.9a*). Presumably, the mono(phosphine) propagating alkylidene species (*Figure 3.8a*, **Ia**) decompose in a similar fashion to initiator **A** once all the monomer has been consumed.[2]

3.3.1.2 Molecular Weight Distribution of Recovered Polymer

Samples of poly(**12b**) recovered from polymerisations mediated by initiator **A** and initiator **F** were found to be insoluble in the solvents suitable for performing GPC analysis. Therefore, molecular weight data of these materials could not been obtained. The inherent lack of solubility of the polymers may be due to cross-linking, which is thought to arise from ring opening metathesis (ROM) of the cyclopentene units contained within the polymer backbone (*Figure 3.10*).[10]

The polydispersity of poly(**1**) recovered from ROMP mediated by initiator **F** was found to be very broad, and the value of M_n was larger than anticipated (*Table 3.1*). This is indicative of a ROMP system in which the rate of propagation (k_p) is greater than the rate of initiation (k_i). For the ROMP of the same monomer mediated by initiator **A**, the majority of the initiator was consumed, indicating that the value of k_i was high, and the resulting polymer had a narrower polydispersity and lower molecular weight.

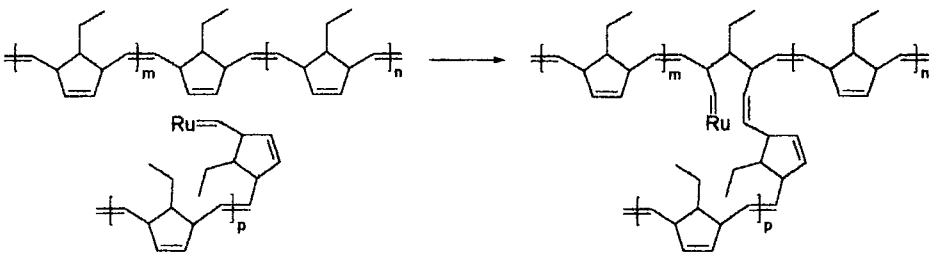


Figure 3.10. Ring opening metathesis between ruthenium alkylidenes and cyclopentene units, which result in a cross-linked polymeric material

3.3.2 ROMP of Monomer 2a

In contrast to monomer **1**, when *exo,endo*-5,6-dicarbomethoxynorbornene (*Figure 2.2*, **2a**) was subjected to ROMP mediated by initiator **A**, the proton resonances for bis(phosphine) propagating species and mono(phosphine) oxygen-chelated propagating species were found to be similar in intensity in the ^{1}H NMR spectra (*cf. Figures 2.18a and 2.19a*).

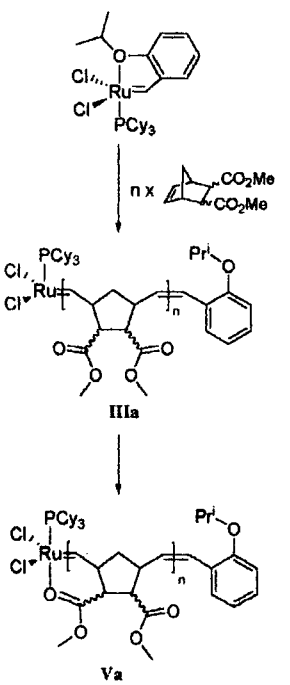


*Figure 3.11. Representation of propagating alkylidene species that form when 5,6-dicarbomethoxynorbornene is subjected to ROMP mediated by initiator **F***

For this reason, the ROMP of monomer **2a** mediated by initiator **F** has been studied, and it was found that, unlike the ROMP of monomer **1**, the alkylidene proton resonances of the mono(phosphine) oxygen-chelated propagating alkylidene species (*Figure 3.11*, **Va**) are pronounced and detectable by ^{1}H NMR spectroscopy at 18.62

and 18.45 ppm (*Figure 3.12a*). This is also attributed to a higher k_i/k_p ratio than for the ROMP of monomer **1** mediated by initiator **F**, which results in 35 % of the initiator being consumed rather than 5 %.

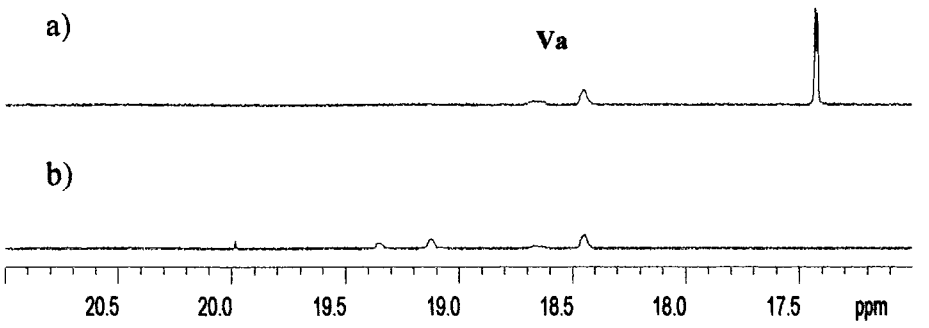


*Figure 3.12. The alkylidene region of 500 MHz ^{1}H NMR spectra ($CDCl_3$) when a) initiator **F**, and b) initiator **A** are used to mediate ROMP of monomer **2a**. $[M]_o/[I]_o=20$*

The mono(phosphine) alkylidene species **IIIa** (*Figure 3.11*) was not observed in the ^{1}H NMR spectra for the ROMP of monomer **2a** mediated by initiator **F** (*Figure 3.12a*). This may be due to **IIIa** being unstable.[1]

3.3.3 Induced Formation of Bis(phosphine) Propagating Species

In order to induce the formation of bis(phosphine) propagating alkylidene species (**IVa**) during the ROMP of monomer **2a** mediated by initiator **F**, a series of reactions were performed. In each system, a known amount of PCy_3 (0-5 equivalents) was added to a solution of initiator **F** ten minutes prior to initiation of the polymerisation. The reactions were followed by ^{1}H NMR spectroscopy until the monomer was completely consumed (*Figure 3.13*). The rate of consumption of monomer **2a** was found to decrease as the amount of added PCy_3 was increased (*Table 3.2*). This was not unexpected, since it is established that addition of free phosphine to ruthenium based ROMP systems reduces the magnitudes of both k_i and k_p.[6]

*Table 3.2. Results for the ROMP of monomer **2a** mediated by initiator **F** in which PCy_3 was added to the initiator prior to polymerisation* [a]

$[PCy_3]_o/[I]_o$	Monomer consumption / hrs	M_n [b,c]	PDI
0	5.5	6,860	1.23
0.1	6	7,658	1.20
0.25	6	6,887	1.27
0.5	7	6,365	1.19
0.75	8.5	6,208	1.20
1	9	6,083	1.15
2	15	3,998	1.24
5	24	3,294	1.25

[a] The reactions were initiated 10 minutes after the addition of PCy_3 to initiator **F** and followed by ^1H NMR spectroscopy. $[M]_o/[I]_o$=20, $[I]_o$=20 mM. [b] the quoted values are relative to polystyrene standards. [c] Predicted M_n = 4,200.

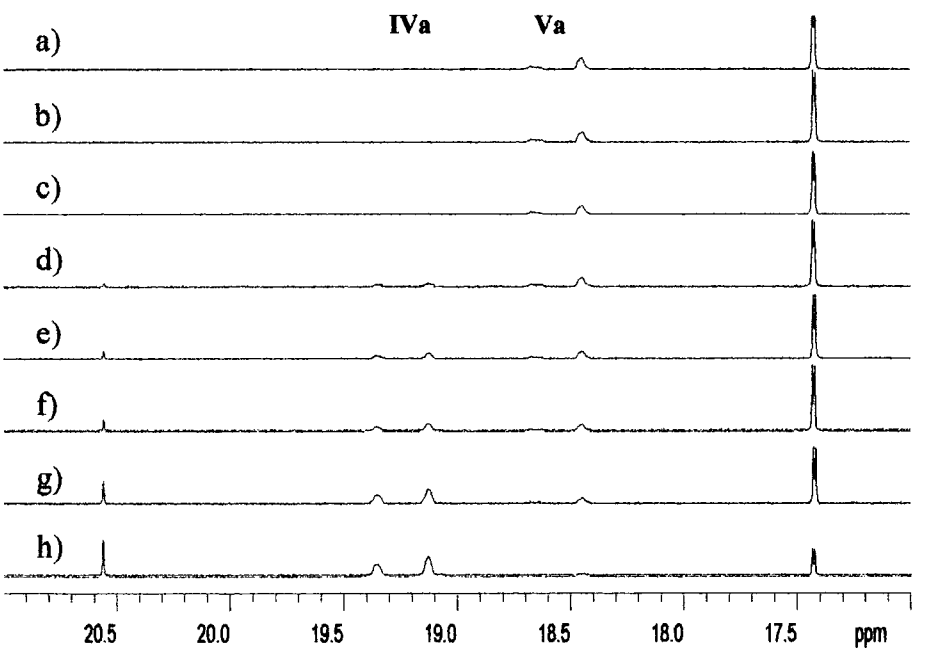


*Figure 3.13. The alkylidene region of 500 MHz ^1H NMR spectra ($CDCl_3$) when **2a** is subjected to ROMP mediated by initiator **F** with a) 0, b) 0.1, c) 0.25, d) 0.5, e) 0.75, f) 1, g) 2 and h) 5 equivalents of PCy_3 added to initiator 10 minutes before polymerisation. $[M]_o/[I]_o$=20, $[I]_o$=20 mM*

In the absence of added PCy_3, the alkylidene region of the ^1H NMR spectrum exhibited resonances for the alkylidene protons of residual initiator **F** (17.44 ppm), and propagating alkylidene species **Va** (18.66 and 18.46 ppm), in which oxygen from the polymer backbone chelates to the ruthenium centre (*Figure 3.13a*).

When PCy_3 was added, the alkylidene proton resonances of initiator **G** were observed (20.55 ppm) alongside those of propagating alkylidene species **IVa** (19.36 and 19.22 ppm) in ^1H NMR spectra (*Figure 3.13*). The additional propagating resonances **IVa** form as a result of the added phosphine displacing the chelating oxygen atom which emanates from the propagating polymer backbone. The alkylidene species **IVa** are analogous to those which arise when initiator **A** is used to mediate the ROMP of monomer **2a**, and the profile of the two resonances are identical (*cf. Figures 3.13h and 3.12b*). As the amount of PCy_3 added to the system was increased, the ratio of **IVa** to **Va** increased accordingly (*Figure 3.13 and 3.14*). In the case of 5 added equivalents of PCy_3, only minor traces of **Va** were present.

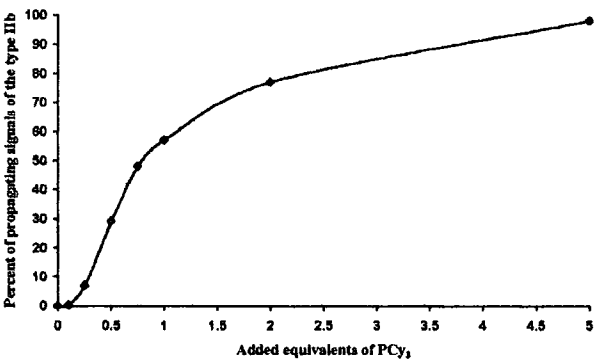


Figure 3.14. A plot showing the percent of ***IVa*** *relative to* ***Va*** *when* ***2a*** *is subjected to ROMP mediated by initiator* ***F*** *in the presence of various PCy_3 concentrations*

An overview of these systems is represented in *Figure 3.15*. The dominant appearance of **IVa** is attributed to the large excess of phosphine in the system converting 50 % of initiator **F** to initiator **G**, and also preventing oxygen from the propagating polymer backbone chelating to the ruthenium centre during the polymerisation. Therefore, k_1, k_{1a} and k_2 become dominant over k_{-1}, k_{-1a} and k_{-2} and hence, **IVa** is the major propagating alkylidene species present.

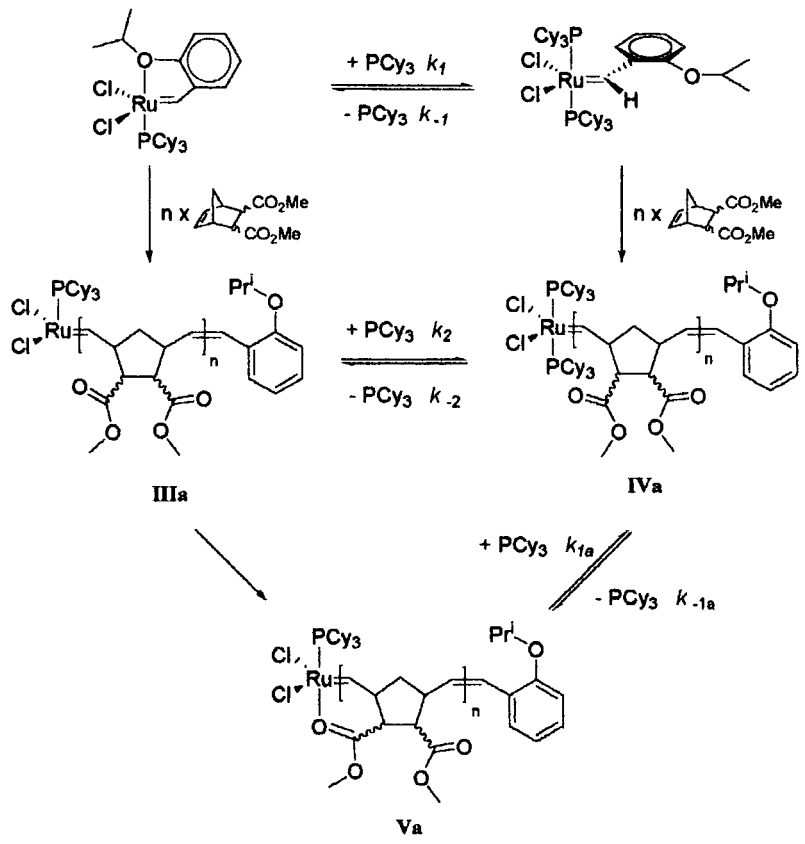


*Figure 3.15. Representation of ruthenium alkylidene species that may form when PCy_3 is added to initiator **F** before it is used to mediate the ROMP of **2a***

In these systems, ethyl vinyl ether was used to terminate the polymerisation reactions once the monomer had been completely consumed, and the polymers were recovered by precipitation into hexane (*Table 3.2*). It was found that as the amount of PCy_3 added to the system was increased from 0 to 5 equivalents, the M_n of the resultant polymer decreased, whereas the polydispersity remained relatively constant. The fall in M_n of the polymers is attributed to the increased concentration of PCy_3 leading to an increase in the ratio of initiator **G** to initiator **F**. In the case of 5 added equivalents of PCy_3, the ratio of initiator **G** to initiator **F** was found to be 50:50 (Section 3.2.3). Earlier, it was demonstrated that for the ROMP of monomer **2a** mediated by initiators **F** and **A**, the consumption of the initiator was 35 % and > 95 %, respectively. This means that as the ratio of initiator **G** to initiator **F** in the system rises, the extent of initiation is enhanced, leading to an increase in the number of active propagating sites. Hence the polymers formed have a lower molecular weight. The PDI remained constant because, in the presence of excess PCy_3, initiators **F** and **G** perform ROMP in a controlled fashion.[6]

3.4 Summary

The observation of regeneration of the initiator during ROMP reactions mediated by initiator **A** is exclusive to bicyclic olefin monomers which contain oxygen-functionalised pendant groups in the 7-position. Regeneration occurs via secondary metathesis reactions at the propagating polymer chain-ends either intra- or inter-molecularly.

In this chapter, an analogy was drawn between $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)$ (**F**), a stable ruthenium alkylidene complex containing internal oxygen-chelation to the ruthenium centre, and species X which appears when 7-alkoxynorbornadiene monomers are subjected to ROMP mediated by initiator **A**. The resonances attributed to alkylidene protons of these species appear at a similar chemical shifts in ^1H NMR spectroscopy, and both are found to be unusually stable in organic media.

Initiator **F** was found to be more stable relative to initiator **A**, and its ligand exchange and ROMP behaviour has been studied. Generally, polymerisation reactions mediated by initiator **F** were found to proceed more slowly than those mediated by initiator **A**, and the extent of initiation was found to be lower. When monomers containing oxygen were subjected to ROMP mediated by initiator **F**, mono(phosphine) propagating alkylidene species were observed. No propagating resonances were observed during the ROMP of a non-oxygen-containing monomer mediated by initiator **F** due to the absence of both oxygen in the polymer backbone and free PCy_3 to chelate to the ruthenium centre. The mono(phosphine) alkylidene propagating species **Ia** and **IIIa** may be unstable on the NMR time-scale.[1]

In the presence of free PCy_3, the chelating oxygen atom of initiator **F** is displaced to give rise to an *iso*-propoxy-substituted benzylidene analogue of initiator **A**. When PCy_3 was added to initiator **F** prior to the polymerisation of monomer **2a**, initiator **G** was observed, and during the polymerisation of monomer **2a** bis(phosphine) propagating species (**IVa**) were seen. As the concentration of added PCy_3 was increased, the intensity of initiator **G** and the bis(phosphine) propagating species (**IVa**) increased at the expense of the initiator **F** and the mono(phosphine) propagating species (**Va**), respectively. The rate of consumption of monomer **2a** decreased with an increase in concentration of PCy_3, and the M_n of the resulting polymer was also affected.

3.5 References

1. J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus, Jr., A. H. Hoveyda, *Journal of the American Chemical Society* **1999**, *121*, 791.
2. M. Ulman, R. H. Grubbs, *Journal of Organic Chemistry* **1999**, *64*, 7202.
3. D. M. Haigh, A. M. Kenwright, E. Khosravi, *Tetrahedron* **2004**, *60*, 7217.
4. S. Demel, W. Schoefberger, C. Slugovc, F. Stelzer, *Journal of Molecular Catalysis A: Chemical* **2003**, *200*, 11.
5. C. Slugovc, S. Demel, S. Riegler, J. Hobisch, F. Stelzer, *Macromolecular Rapid Communications* **2004**, *25*, 475.
6. C. W. Bielawski, R. H. Grubbs, *Macromolecules* **2001**, *34*, 8838.
7. B. R. Maughon, R. H. Grubbs, *Macromolecules* **1997**, *30*, 3459.
8. W. Buchowicz, M. N. Holerca, P. Percec, *Macromolecules* **2001**, *34*, 3842.
9. M. S. Sanford, J. A. Love, R. H. Grubbs, *Journal of the American Chemical Society* **2001**, *123*, 6543.
10. K. J. Ivin, J. C. Mol, *Olefin Metathesis and Metathesis Polymerisation*, Academic, San Diego, **1997**.

Chapter 4

Probing the Nature of Propagating Species that arise during ROMP Mediated by Initiator A and their Effect on the Regeneration Process

4.1 Introduction

In Chapter 3, the ligand exchange and ROMP activity of $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)$ (*Figure 3.1*, **F**) was studied and it was compared to the stable alkylidene resonances (species X) observed in the alkylidene region of ^1H NMR spectra obtained during the ROMP of 7-alkoxynorbornadiene monomers. Initiator **F**, contains internal oxygen chelation to the ruthenium centre and, unlike $RuCl_2(PCy_3)_2(=CHPh)$ (*Figure 2.1*, **A**), it is extremely stable in organic media. The alkylidene proton resonance of both initiator **A** and species X appear at ~ 17.5 ppm in ^1H NMR spectroscopy.

Recent publications focus on the identity of propagating alkylidene species that arise when initiator **A** is used to mediate ROMP.[1-5] This chapter reports a variety of ROMP reactions mediated by initiator **A**, including that of monomer **1** (*Figure 2.2*). Free phosphines and phosphine scavengers are employed to probe the identity of the propagating alkylidene species that arise. The results lead to improved characterisation of the propagating alkylidene species formed, and allow the prediction of the chemical shift at which these species are likely to appear in ^1H NMR spectra of related systems.

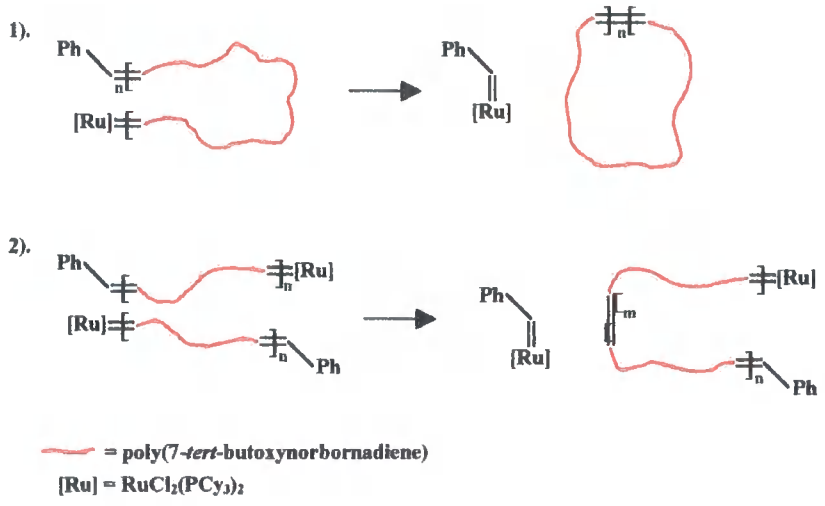


Figure 4.1. Secondary metathesis reactions that lead to regeneration of the initiator by 1) intramolecular reactions, or 2) intermolecular reactions

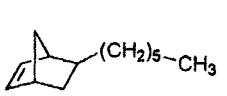
As discussed in chapter 2, regeneration of the initiator is observed when monomer **1** is subjected to ROMP mediated by initiator **A**.[6-8] In order for regeneration of the initiator to occur, the terminal double bonds of propagating polymer chains must

come into close proximity and undergo a secondary metathesis (backbiting) reaction. This can occur by two mechanisms (*Figure 4.1*).

It is believed that chelation of an oxygen atom from the propagating polymer chain end to the ruthenium centre (either intra- or intermolecularly), brings terminal double bonds into the close proximity of the ruthenium alkylidene, and hence encourages secondary metathesis reactions which result in regeneration of the initiator (*Figure 2.15).*

The mechanisms by which regeneration of the initiator occurs is studied in detail, and the role of the pendant 7-*tert*-butoxy groups in the regeneration process, when monomer **1** is subjected to ROMP mediated by initiator **A**, is investigated. Proof for the existence of both oxygen chelation to the ruthenium centre and secondary metathesis (backbiting) reactions, as well as their co-existence, is provided in this chapter, lending support to the hypothesis that chelation of oxygen to the ruthenium centre does facilitate the regeneration process.

The chemical structure of the ruthenium alkylidene complexes and the bicyclic monomers discussed in this chapter are depicted in *Figures 2.1, 2.2, 3.1* and *4.2*.



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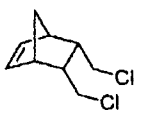

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Figure 4.2. exo-5-hexylnorbornene [13] and endo,endo-5,6-bis(chloromethyl)norbornene [14]

4.2 The Identity of Propagating Species that arise during the ROMP of Bicyclic Monomers Mediated by Initiator A

It is recognised that secondary metathesis reactions may occur either intra- or inter-molecularly along the propagating polymer backbone when monomer **1** is subjected to ROMP mediated by initiator **A** (*Figure 4.1*). It is believed that secondary metathesis reactions which result in regeneration of the initiator may be facilitated by chelation of oxygen from the chain-end of the propagating polymer species to the ruthenium centre (*Figure 2.15*).

As highlighted in chapter 2, when monomer **1** is subjected to ROMP mediated by initiator **A**, two types of propagating species are seen in the alkylidene region of the ^{1}H NMR spectra (*Figure 2.10*). The resonance labelled P_n (t, 19.36 ppm), was assigned to alkylidene protons of bis(phosphine) propagating species, and the broad resonance labelled X (~17.5 ppm), was attributed to protons of a mono(phosphine) species in which a labile phosphine ligand is displaced by a chelating oxygen atom emanating from the propagating polymer backbone. It is established that the appearance of three propagating signals (P_n) arises due to the sensitivity of the chemical shift of the alkylidene proton to the *cis/trans* isomerism of the adjacent double bond and to the *meso/racemic* isomerism of the adjacent dyad.[8] Conversely, no direct evidence is provided in support of the structure of species X. This section conclusively determines the identity of species X, and also the nature of propagating alkylidene species that arise in related ROMP reactions mediated by initiator **A**.

4.2.1 The Effect of the Pendant Functional Groups of Bicyclic Monomers

Analysis of the alkylidene region of ^{1}H NMR spectra, obtained from the ROMP of the three possible stereo isomers of 5,6-dicarbomethoxynorbornene [*exo,endo*; *exo,exo*; *endo,endo* (*Figure 2.2*, **2a-c**)] mediated by initiator **A**, clearly highlights the sensitivity of the chemical shift and multiplicity of propagating alkylidene proton resonances to the specific position and functionality of the pendant groups contained within the monomer unit. As highlighted in *Figure 4.3*, two distinct sets of propagating alkylidene signals (**IVb** and **Vb**) arise in the ^{1}H NMR spectra for each ROMP reaction.

The appearance of the propagating alkylidene resonances for each monomer was markedly different, and this was attributed to the specific orientation of the pendant groups contained within the monomer units. A subtle structural difference of the monomer was also found to impact other aspects of the polymerisation process, including rate of monomer consumption and extent of initiation. This implies that the specific orientation of the pendant functional groups of a monomer can influence the relative rates of initiation (k_i) and propagation (k_p) during a ROMP reaction mediated by initiator **A** (*Table 4.1*).

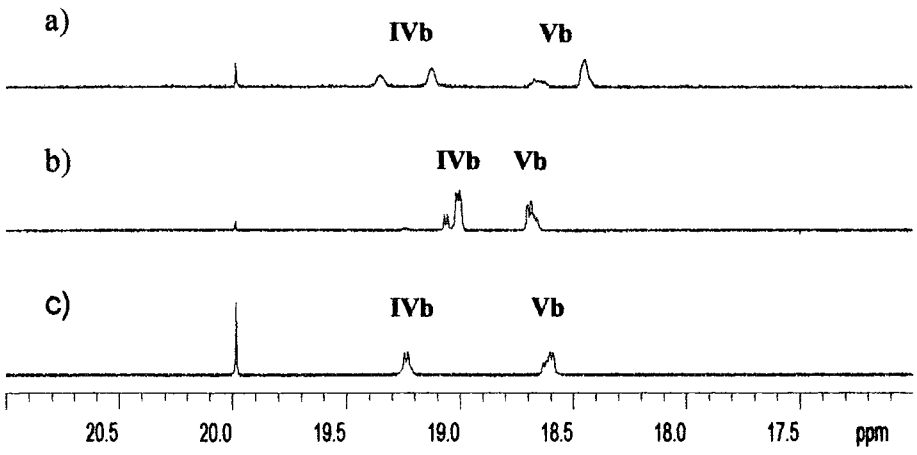

*Figure 4.3. The alkylidene region of 500 MHz ^1H NMR spectra ($CDCl_3$) when a) **2a**, b) **2b** and c) **2c** are subjected to ROMP mediated by initiator **A**. $[M]_o/[I]_o=20$, $[I]_o=15$ mM*

*Table 4.1. Results of the ROMP of the three isomers of 5,6-dicarbomethoxynorbornene (**2a-c**) mediated by initiator **A** [a]*

Monomer	Monomer consumption / hrs	Extent of initiation / %
2a	3	94
2b	0.5	97
2c	4	76

[a] Polymerisations were performed in $CDCl_3$ at ambient temperature and were mediated by initiator **A** with $[I]_o$=15 mM. The reactions were followed by ^1H NMR spectroscopy.

In order to fully understand the processes of initiation and propagation during ROMP reactions mediated by initiator **A**, it is necessary to determine the structural identity of the species that give rise to propagating alkylidene resonances apparent in the ^1H NMR spectra.

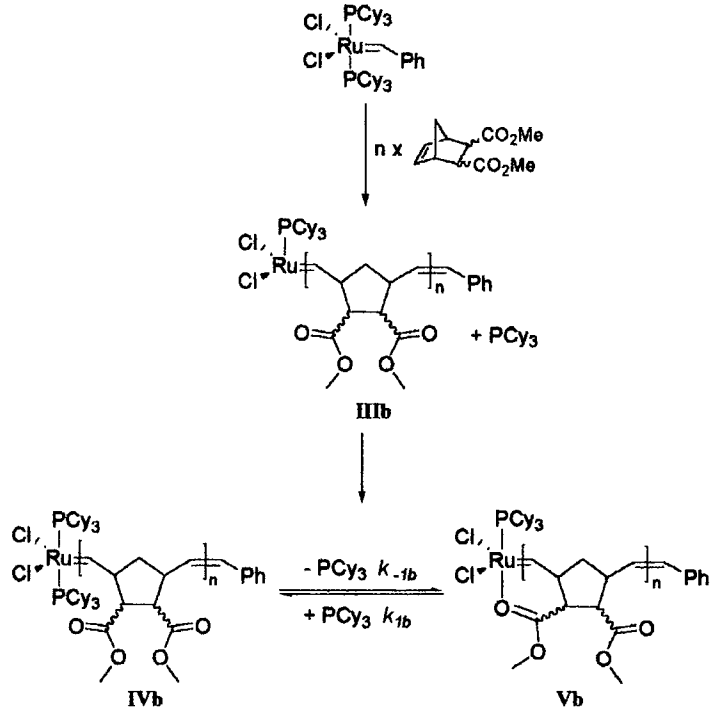

Figure 4.4. Representation of the propagating alkylidene species that may form when the ROMP of 5,6-dicarbomethoxynorbornene is mediated by initiator A

Consideration of the mechanism by which the ROMP of 5,6-dicarbomethoxynorbornenes mediated by initiator **A** proceed, reveals that immediately after the insertion of a monomer unit, the ruthenium propagating alkylidene (**IIIb**) has a vacant co-ordination site (*Figure 4.4*). This site can be occupied by either free PCy_3 (which dissociated from the ruthenium centre in order to generate the active site) to give rise to bis(phosphine) propagating alkylidene species of the type **IVb** (*Figure 4.4*). Alternatively, an oxygen atom emanating from the polymer backbone can chelate to the ruthenium centre, giving rise to propagating mono(phosphine) alkylidene species of the type **Vb** (*Figure 4.4*). The alkylidene proton resonances for propagating species of the type **IVb** and **Vb** have been assigned to signals observed in the ^1H NMR spectra obtained during the ROMP of the three isomers of 5,6-dicarbomethoxynorbornene mediated by initiator **A** (*Figure 4.3*).

The intensity of **IVb** or **Vb** observed during a ROMP reaction depends on the relative values of k_{1b} and k_{-1b}, which reflect the preference of either PCy_3 or oxygen from the polymer backbone to co-ordinate to the ruthenium centre (*Figure 4.4*).

4.2.2 Verification of the Structure of Bis(phosphine) Propagating Species

The identity of **IVb** and **Vb** has been confirmed by the addition of either free phosphine or a phosphine scavenger to the ROMP system upon complete consumption of the monomer.

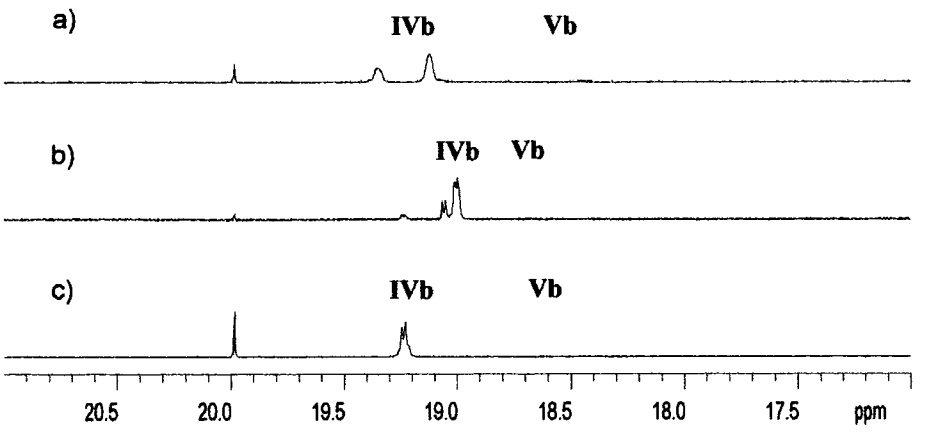

*Figure 4.5. The alkylidene region of 500 MHz ^1H NMR spectra ($CDCl_3$) for the ROMP of, a) **2a**, b) **2b**, and c) **2c** mediated by initiator **A**, in the presence of 5 equivalents of PCy_3. $[M]_o/[I]_o=20$, $[I]_o=15$ mM*

The addition of 5 equivalents of PCy_3 to the ROMP reactions of the three isomers of 5,6-dicarbomethoxynorbornene (**2a-c**) mediated by initiator **A**, once the polymerisation has reached completion, resulted in minor traces of propagating species **Vb** being observed in the ^1H NMR spectra, and species **IVb** became dominant (*Figure 4.5*). The addition of the large excess of free phosphine saturated the ROMP system and enhanced k_{1b} relative to k_{-1b}, hence resulting in the displacement of the chelating oxygen atom of **Vb** by PCy_3 (*Figure 4.4*).

4.2.3 Verification of the Structure of Mono(phosphine) Oxygen Chelated Propagating Species

It is established that CuCl is able to act as a 'phosphine sponge' by undergoing reaction with free phosphines to form marginally soluble, ill-defined complexes.[9] When CuCl is added to ROMP reactions mediated by initiator **A**, labile PCy_3 ligands become 'trapped'. This generates a vacant coordination site on the ruthenium centre, allowing oxygen in the polymer backbone to chelate. The addition of CuCl to the ROMP of 5,6-dicarbomethoxynorbornenes mediated by initiator **A**, effectively

eliminated k_{1b} (*Figure 4.4*). Therefore, only propagating species of the type **Vb** were observed in ^{1}H NMR spectra (*Figure 4.6*).

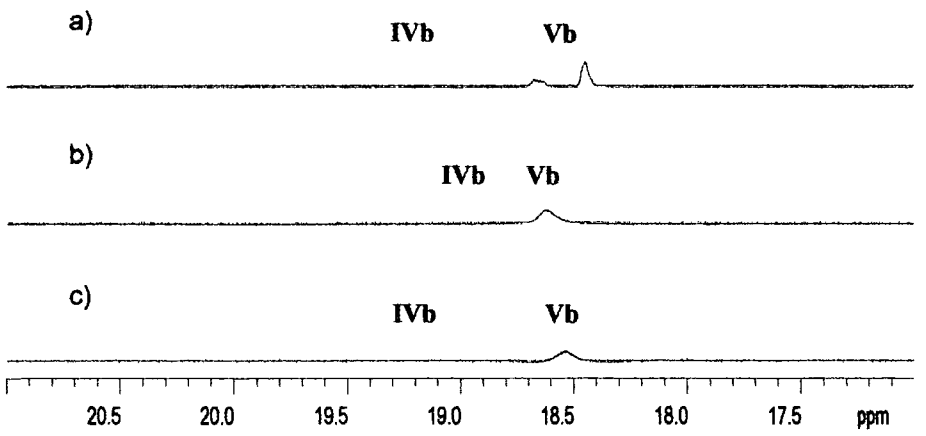

Figure 4.6. The alkylidene region of 500 MHz ^{1}H NMR spectra ($CDCl_3$) for the ROMP of, a) ***2a****, b)* ***2b****, and c)* ***2c*** *mediated by initiator* ***A****, in the presence of 10 equivalents CuCl. $[M]_o/[I]_o$=20, $[I]_o$=15 mM*

4.2.4 Structural Identity of Propagating Species for ROMP of a Range of Bicyclic Olefin Monomers

The observations described above, prompted the study of propagating species that arise during the ROMP of other bicyclic olefin monomers containing oxygen (*Figure 2.2*, **3a**, **3b**, **8** and **9**) mediated by initiator **A**. In chapter 2, the ROMP reactions of these monomers mediated by initiator **A** were studied in order to establish whether regeneration of the initiator occurred in any of these systems.[6] It did not. However, it is now recognised that two types of propagating species were apparent in all of the systems; bis(phosphine) alkylidene species (*Figure 4.7, structure* **VIb**) and mono(phosphine) oxygen-chelated alkylidene species (*Figure 4.7, structure* **VIIb**).

The alkylidene region of the ^{1}H NMR spectra obtained during the ROMP of monomers **3a**, **3b**, **8** and **9** are shown in *Figure 4.8* and the resonances attributed to propagating species of the type **VIb** and **VIIb** are indicated. The identity of species **VIb** and **VIIb** was confirmed by the addition of PCy_3 or CuCl to the ROMP reactions of these monomers in the same manner as described previously.

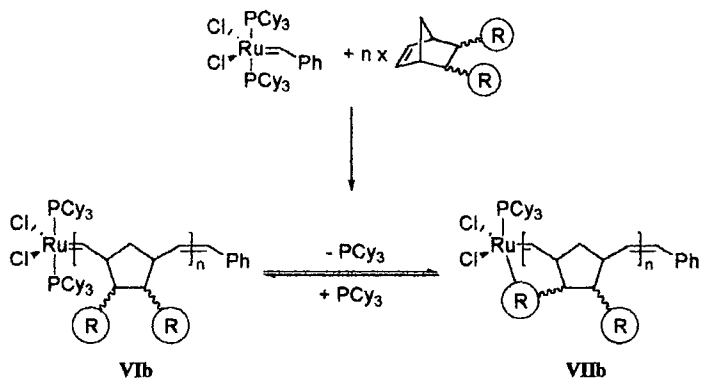

*Figure 4.7. The propagating alkylidene species that may form when the ROMP of oxygen functionalised 5,6-substituted bicyclic monomers is mediated by initiator **A** (R substituent contains oxygen)*

The alkylidene region of the ^{1}H NMR spectra when either 5 equivalents of PCy_3 or 10 equivalents of CuCl were added to the ROMP of these oxygen containing monomers mediated by initiator **A** are shown in *Figures 4.9* and *4.10*, respectively.

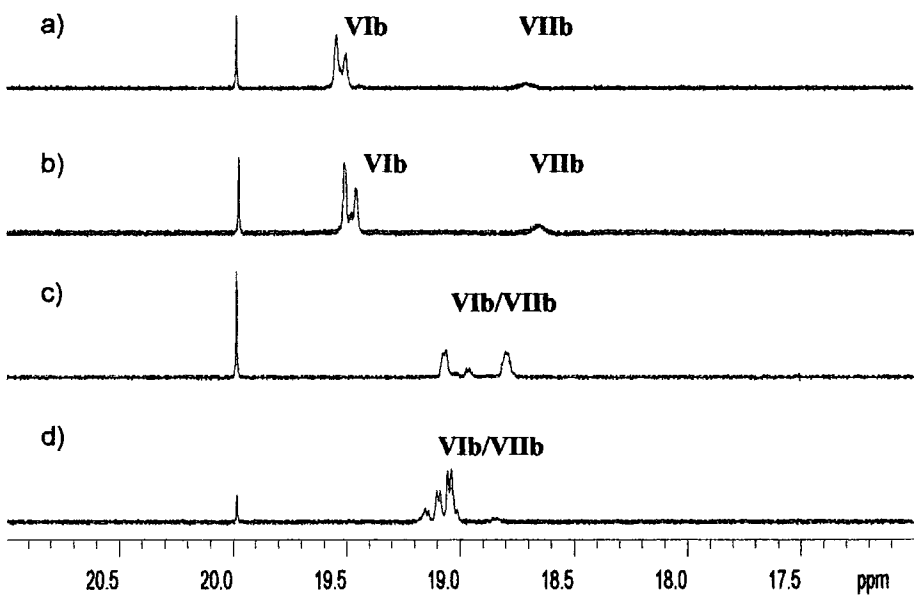

*Figure 4.8. The alkylidene region of 500 MHz ^{1}H NMR spectra ($CDCl_3$) for ROMP of a) **3a**, b) **3b**, c) **8**, and d) **9** mediated by initiator **A**. $[M]_o/[I]_o$=50, $[I]_o$=15 mM*

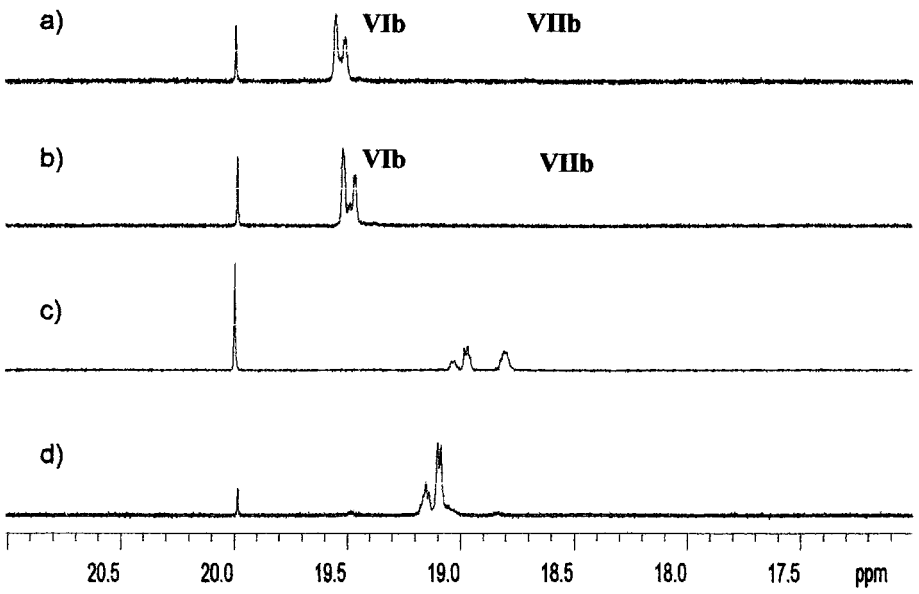

*Figure 4.9. The alkylidene region of 500 MHz ^{1}H NMR spectra ($CDCl_3$) for the ROMP of a) **3a**, b) **3b**, c) **8**, and d) **9** mediated by initiator **A**, in the presence of 5 equivalents of PCy_3. $[M]_o/[I]_o$=50, $[I]_o$=15 mM*

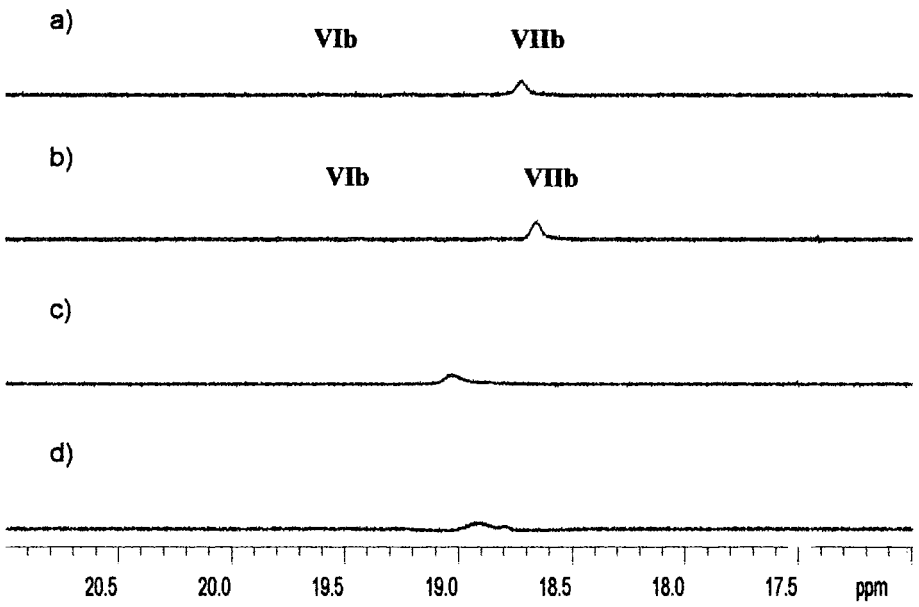

*Figure 4.10. The alkylidene region of 500 MHz ^{1}H NMR spectra ($CDCl_3$) for the ROMP of a) **3a**, b) **3b**, c) **8**, and d) **9** mediated by initiator **A**, in the presence of 10 equivalents of CuCl. $[M]_o/[I]_o$=50, $[I]_o$=15 mM*

In the case of the ROMP of monomers **3a** and **3b**, the resonances at 19.52 and 19.48 ppm, respectively (*Figure 4.8*), are assigned to bis(phosphine) species of the type

VIb, on the basis that their intensity increased upon the addition of PCy_3 and that they disappeared upon the addition of CuCl (*Figures 4.9 and 4.10*). The broad resonances at 18.70 and 18.65 ppm, respectively (*Figure 4.8*), displayed the opposite behaviour when either PCy_3 or CuCl was added to the system (*Figures 4.9 and 4.10*), and hence they were assigned to propagating mono(phosphine) alkylidene species of the type **VIIb**.

When PCy_3 or CuCl was added to the ROMP reactions of monomers **8** and **9** mediated by initiator **A**, the relative intensity and appearance of the propagating species in ^{1}H NMR spectra were seen to change (*cf. Figures 4.8, 4.9 and 4.10*). This suggests the presence of propagating bis(phosphine) alkylidene species of the type, **VIb**, as well as those which contain oxygen chelation from the polymer backbone to the ruthenium centre, **VIIb**. However, the identity of these distinctly different propagating structures could not be conclusively determined, possibly due to the effects of rapid ligand exchange.

4.2.5 ROMP of Non-Oxygen-Containing Monomers

In light of the above mentioned observations, it was anticipated that during the ROMP of non-oxygen-containing bicyclic olefin monomers mediated by initiator **A**, only one set of propagating alkylidene resonances, corresponding to bis(phosphine) species **VIb**, would be observed by ^{1}H NMR spectroscopy. This phenomenon was investigated by performing the ROMP of non-oxygen-containing monomers **4** and **12-14** (*Figures 2.2, 3.1 and 4.2*) mediated by initiator **A**. The alkylidene regions of the ^{1}H NMR spectra for the polymerisation of these monomers are shown in *Figures 4.11* and *4.12*.

In all of these ROMP reactions, a resonance is observed for the alkylidene proton of residual initiator **A** (19.99 ppm). The chemical shift and multiplicity of the propagating alkylidene proton resonances in each system is dependent on the nature and position of the functionalities contained within the monomer units. In the case of monomers **12a**-c it is noticeable that a minor change in the steric bulk of the 7-alkyl group has a significant effect on the appearance of the propagating alkylidene proton resonances (*Figure 4.11*). The propagating alkylidene signals for monomers **12a**, **12b** and **12c** appear as multiplets at (19.21 and 19.05 ppm), (18.92 and 18.80 ppm) and (19.02, 18.96 and 18.89 ppm), respectively. For monomers **4**, **13** and **14** the

propagating alkylidene proton resonances are observed as multiplets at (18.78 ppm), (18.80 ppm) and (19.44 and 19.48 ppm), respectively (*Figure 4.12*).

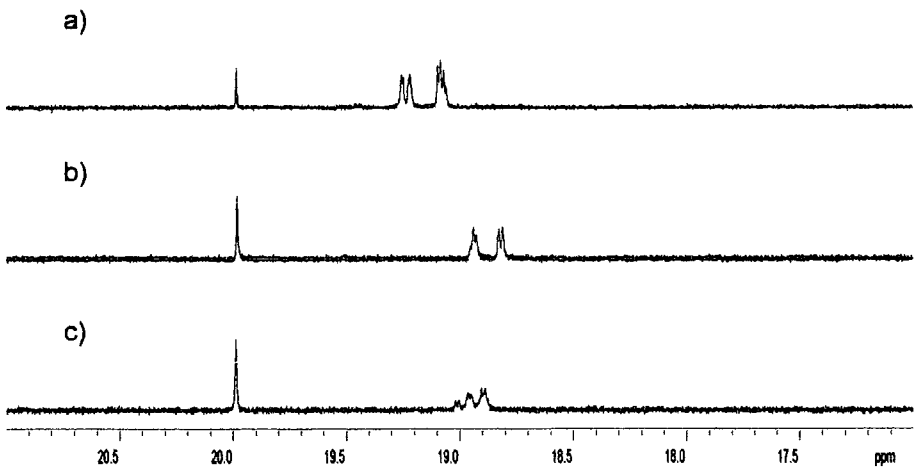

Figure 4.11. The alkylidene region of 500 MHz ^{1}H NMR spectra ($CDCl_3$) for the ROMP of a) ***12a****, b)* ***12b****, and c)* ***12c*** *mediated by initiator* ***A****. $[M]_o/[I]_o$=50, $[I]_o$=15 mM*

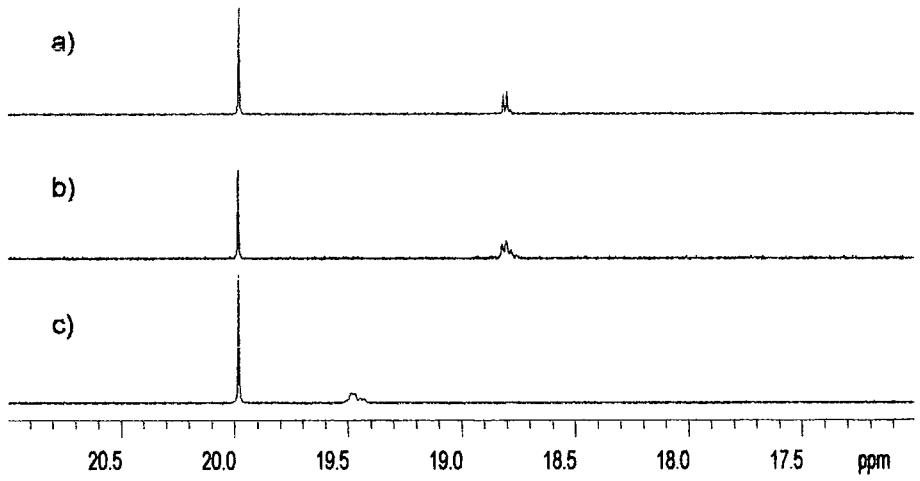

Figure 4.12. The alkylidene region of the 500 MHz ^{1}H NMR spectra ($CDCl_3$) for ROMP of a) ***4****, b)* ***13****, and c)* ***14****, mediated by initiator* ***A****. $[M]_o/[I]_o$=50, $[I]_o$=15 mM*

In some cases, the alkylidene region of the ^{1}H NMR spectra of these ROMP systems exhibit more than one propagating signal, but it has been shown that all the resonances present are attributed to bis(phosphine) propagating alkylidene species. This was achieved by the addition of either PCy_3 or CuCl to the systems once the

monomer had been consumed. In all of the systems the appearance of the alkylidene region of the ^{1}H NMR spectra remained unchanged upon the addition of PCy_3. However, all of the alkylidene signals disappeared when CuCl was added, confirming that the propagating species were bis(phosphine) and not mono(phosphine). As an example of this behaviour, the change in the appearance of the alkylidene region of ^{1}H NMR spectra when PCy_3 and CuCl were added to the ROMP of **12a** mediated by initiator **A** are shown in *Figure 4.13*.

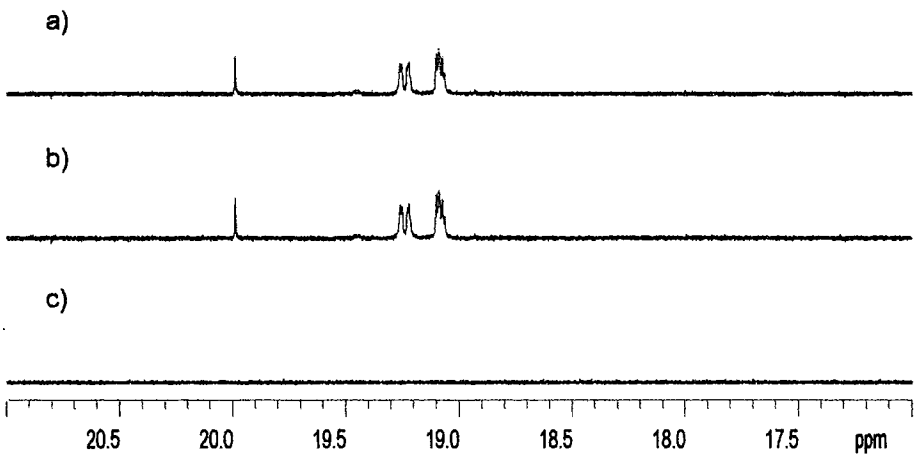

*Figure 4.13. The alkylidene region of 500 MHz ^{1}H NMR spectra ($CDCl_3$) 1 hour after a) initiation of the ROMP of monomer **12a** by initiator **A**, b) with 5 added equivalents of PCy_3, and c) with 10 added equivalents of CuCl. $[M]_o/[I]_o$=50, $[I]_o$=15 mM*

It is of interest that the propagating alkylidene species that arise during the ROMP of monomers **4** and **12-14** are relatively unstable in solution, and no alkylidene resonances are present after 75 hours of reaction. This is consistent with the stability of ruthenium alkylidene species being enhanced by the presence of oxygen chelation to the metal centre (Section 3.2.2).

4.2.6 Verification of the Structure of Propagating Species for the ROMP of Monomer 1

The phenomenon of regeneration when monomer **1** is subjected to ROMP mediated by initiator **A**, is attributed to secondary metathesis reactions at the propagating polymer chain ends, which are believed to be facilitated by the formation of oxygen-chelated ruthenium alkylidene species (*Figure 2.15*).

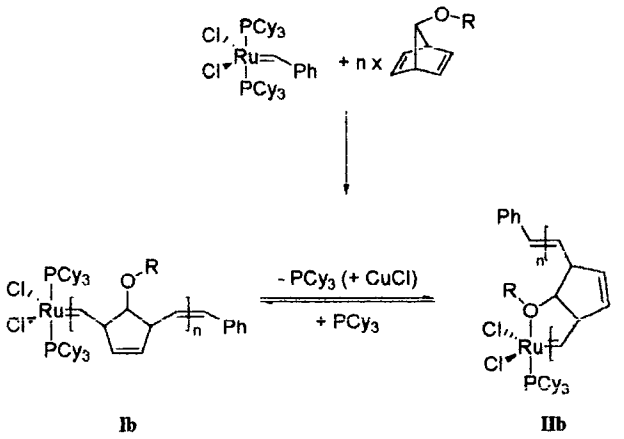

Figure 4.14. Representation of propagating alkylidene species that may form when the ROMP of monomer 1 is mediated by initiator A

In chapter 2, the two propagating alkylidene resonances that arise at 19.36 ppm (t) and ~17.5 ppm (br.) in the ^{1}H NMR spectra during the ROMP of monomer **1** mediated by initiator **A**, were labelled P_n and X, respectively (*Figure 2.10*). Based on the observations described earlier in this chapter, it was possible to determine whether the nature of these propagating species was bis(phosphine) (**Ib**) or mono(phosphine) oxygen chelated (**IIb**) (*Figure 4.14*). The addition of either PCy_3 or CuCl to the ROMP of monomer **1** mediated by initiator **A** after 3 hours of reaction conclusively revealed their identity.

When 5 equivalents of PCy_3 were added to the reaction, species X noticeably diminished in intensity and P_n became more pronounced (*Figure 4.15b*). Conversely, when 10 equivalents of CuCl were added to the reaction, P_n disappeared and X increased in intensity (*Figure 4.15c*). These observations indicate that the alkylidene protons of P_n are attributed to bis(phosphine) propagating species of the type **Ib**, whereas those of species X are attributed to propagating species of the type **IIb** in which oxygen from the polymer backbone chelates to the ruthenium centre (*Figure 4.14*). The relative intensity of **Ib** to **IIb** (16:1), deduced from ^{1}H NMR spectra before the addition of either PCy_3 or CuCl, indicates that in this system, association of PCy_3 to the ruthenium centre is preferred over chelation from oxygen in the propagating polymer backbone.

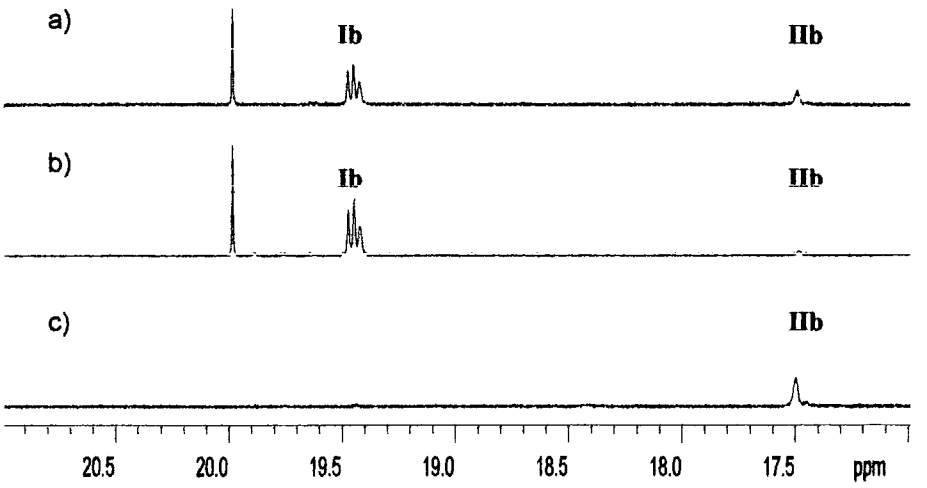

*Figure 4.15. The alkylidene region of 500 MHz ^{1}H NMR spectra ($CDCl_3$) 3 hours after a) initiation of the ROMP of monomer **1** by initiator **A**, b) with 5 added equivalents of PCy_3, and c) with 10 added equivalents of CuCl. $[M]_o/[I]_o$=50, $[I]_o$=15 mM*

The relatively low frequency chemical shift observed for the oxygen-chelated propagating species, **IIb**, is worthy of comment. The chemical shift of ~17.5 ppm is much lower than that observed for any other oxygen-containing monomer studied in this chapter, and it is similar to that observed for the alkylidene proton of initiator **F** (17.44 ppm), in which chelation of ethereal oxygen to the ruthenium centre results in the formation of a 5-membered ring (Section 3.2). This suggests that resonance **IIb** is due to chelation of the monomer closest to the ruthenium centre via a 5-membered ring, rather than to an oxygen further down the polymer chain, and this may be significant in explaining the anomalous behaviour observed during the ROMP of 7-alkoxynorbornadienes.[6] This is discussed further in Section 4.4.1.

4.2.7 Summary of Propagating Alkylidene Species Apparent for ROMP Reactions Mediated by Initiator A

The propagating alkylidene species for the ROMP of bicyclic olefins mediated by initiator **A** are summarised in *Figure 4.16*. It reiterates that pendant functional groups contained within the monomer unit, dictate the appearance of the propagating alkylidene species that arise in the ^{1}H NMR spectra.

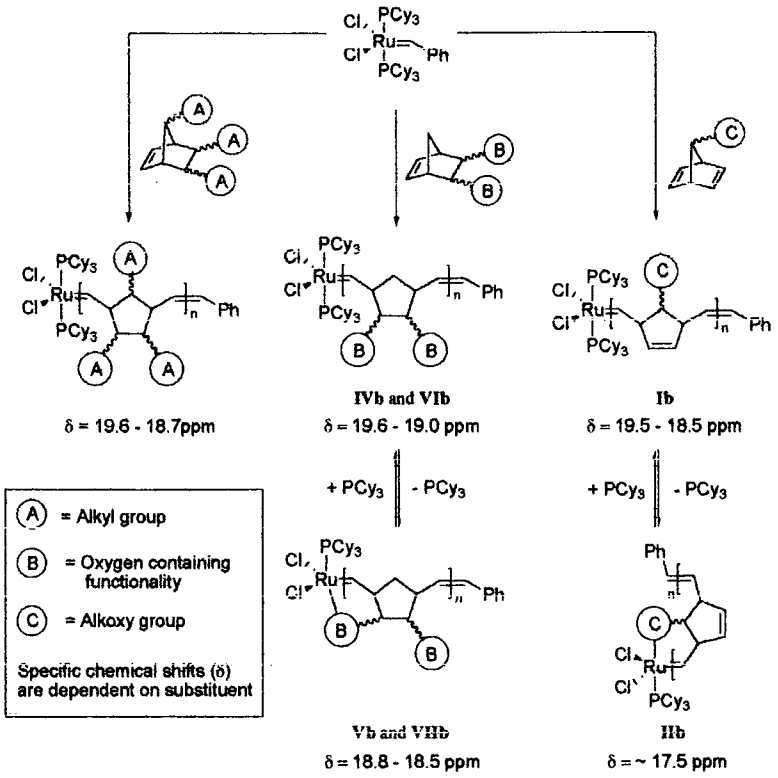

*Figure 4.16. A summary of propagating alkylidene species that arise in the ^{1}H NMR spectra during the ROMP of bicyclic olefins mediated by initiator **A**. The quoted chemical shifts are those of the alkylidene resonance*

In all cases, alongside residual initiator **A**, the alkylidene proton of bis(phosphine) propagating species are apparent at 19.6–18.5 ppm (the exact chemical shift depends on the specific position and nature of the pendant functional groups). If the monomer does not contain oxygen, then these are the only propagating species observed by ^{1}H NMR spectroscopy.

If the monomer does contain oxygen-functionalised pendant groups, then additional resonances are observed. These are attributed to the alkylidene protons of mono(phosphine) species in which oxygen in the propagating backbone chelates to the ruthenium centre. This type of species appears at 18.8-18.4 ppm or ~17.5 ppm depending on the specific position and functionality of the pendant groups.[6]

In a recent publication, we proposed that chelation of oxygen from the propagating polymer backbone to the ruthenium centre promotes regeneration of the initiator.[6] The results above clearly show that oxygen chelation in ROMP systems does not necessarily result in regeneration of the initiator. However, if the monomer

specifically contains oxygen attached to the 7-position, then regeneration of the initiator may be observed.[6]

4.3 Proposed Mechanisms by which Secondary Metathesis (backbiting) Reactions Occur

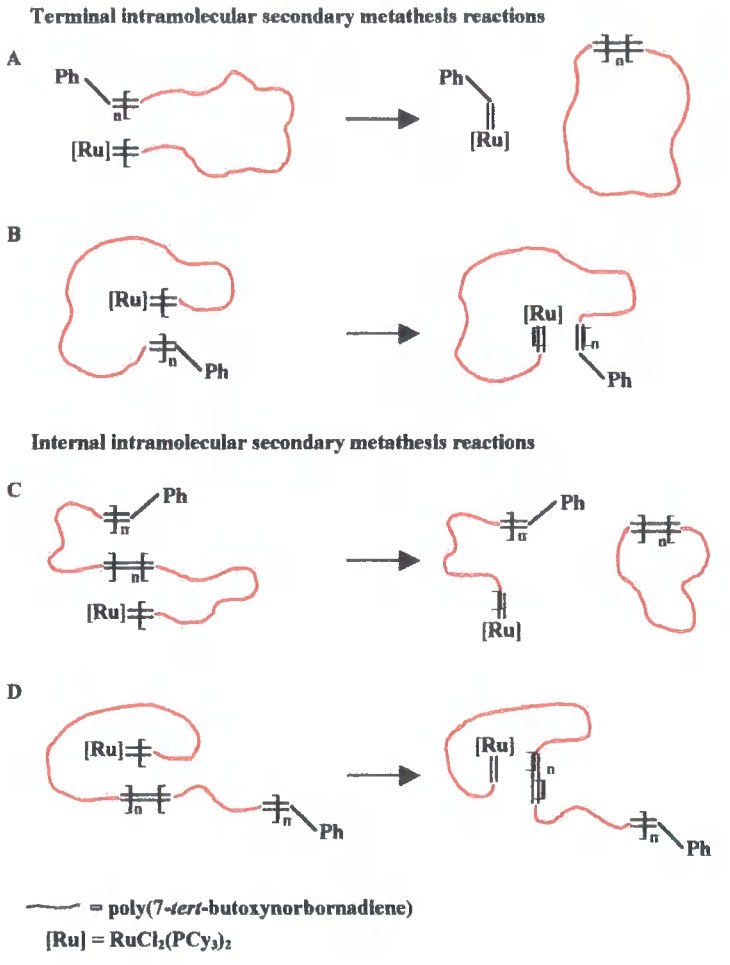

*Figure 4.17. Intramolecular secondary metathesis reactions that can occur when **1** is subjected to ROMP mediated by initiator **A***

Although there are only two backbiting mechanisms by which regeneration of the initiator occurs (*Figure 4.1*), these are not the only secondary metathesis reactions that can occur between the ruthenium alkylidene and double bonds contained within the propagating polymer backbone. It is possible for backbiting reactions to take place randomly intra- or inter-molecularly anywhere along the propagating polymer backbone. Including the two mechanisms that lead to regeneration of the initiator (**A** and **E**), there are in total nine types of secondary metathesis reactions (**A-I**). These

intra- (**A-D**) and inter-molecular (**E-I**) reactions are illustrated in *Figures 4.17* and *4.18*, respectively.

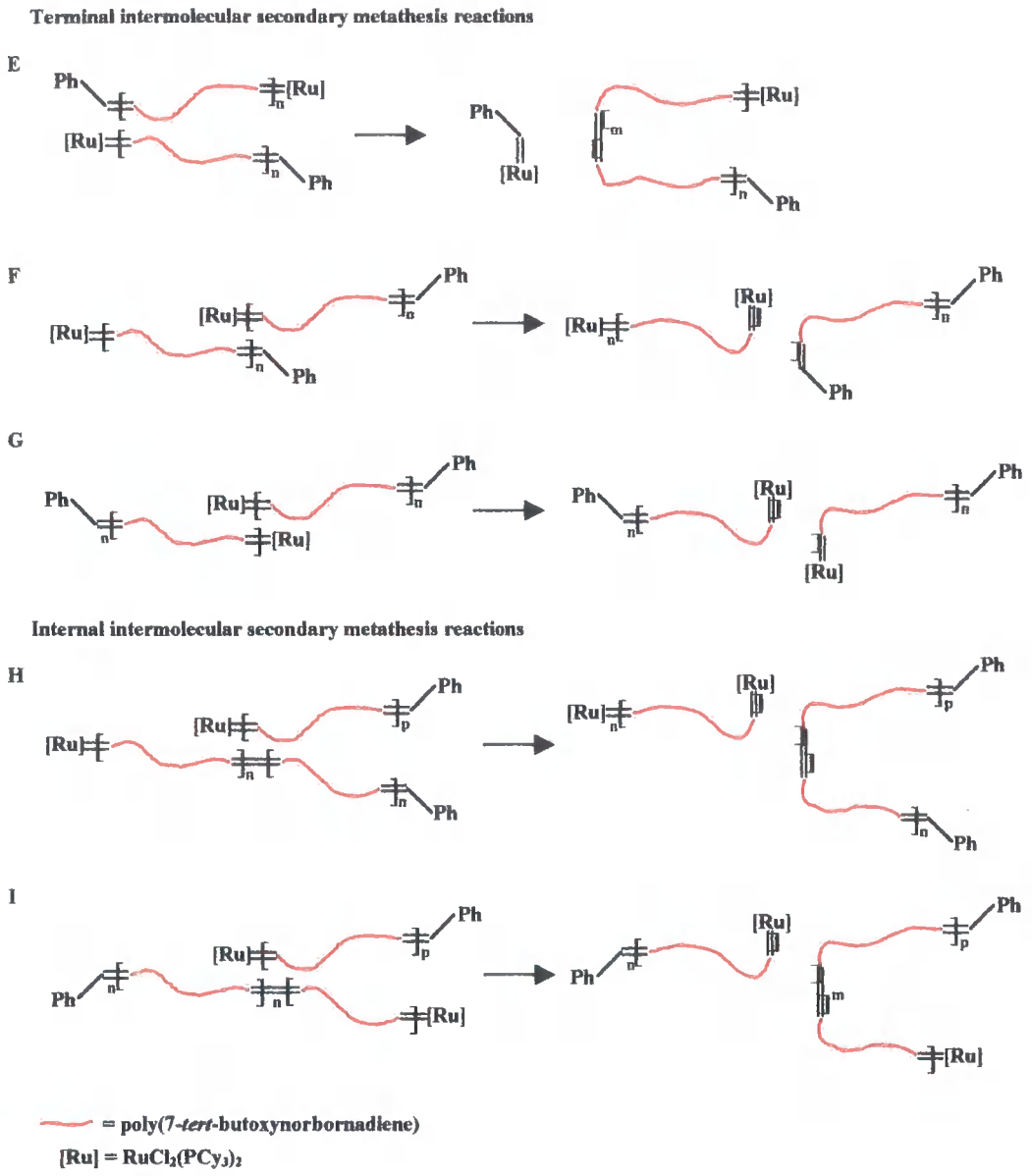

*Figure 4.18. Intermolecular secondary metathesis reactions that can occur when **1** is subjected to ROMP mediated by initiator **A***

Four of the outlined backbiting reactions (**C**, **E**, **H** and **I**) result in broadening the molecular weight distribution of poly(**1**), and two lead to the formation of cyclic poly(**1**) (**A** and **C**). Mechanisms **B**, **D**, **F** and **G** have no effect on the overall distribution of molecular weights, they simply redistribute the monomer units contained within the propagating polymer chain. The cumulative affect of these secondary metathesis reactions is significant broadening of the molecular weight distribution of poly(**1**).

In order to demonstrate that secondary metathesis reactions do occur during the ROMP of monomer **1** mediated by initiator **A**, a series of experiments were performed.

4.3.1 Block copolymerisation of 7-alkoxy and 7-alkyl Norbornadienes

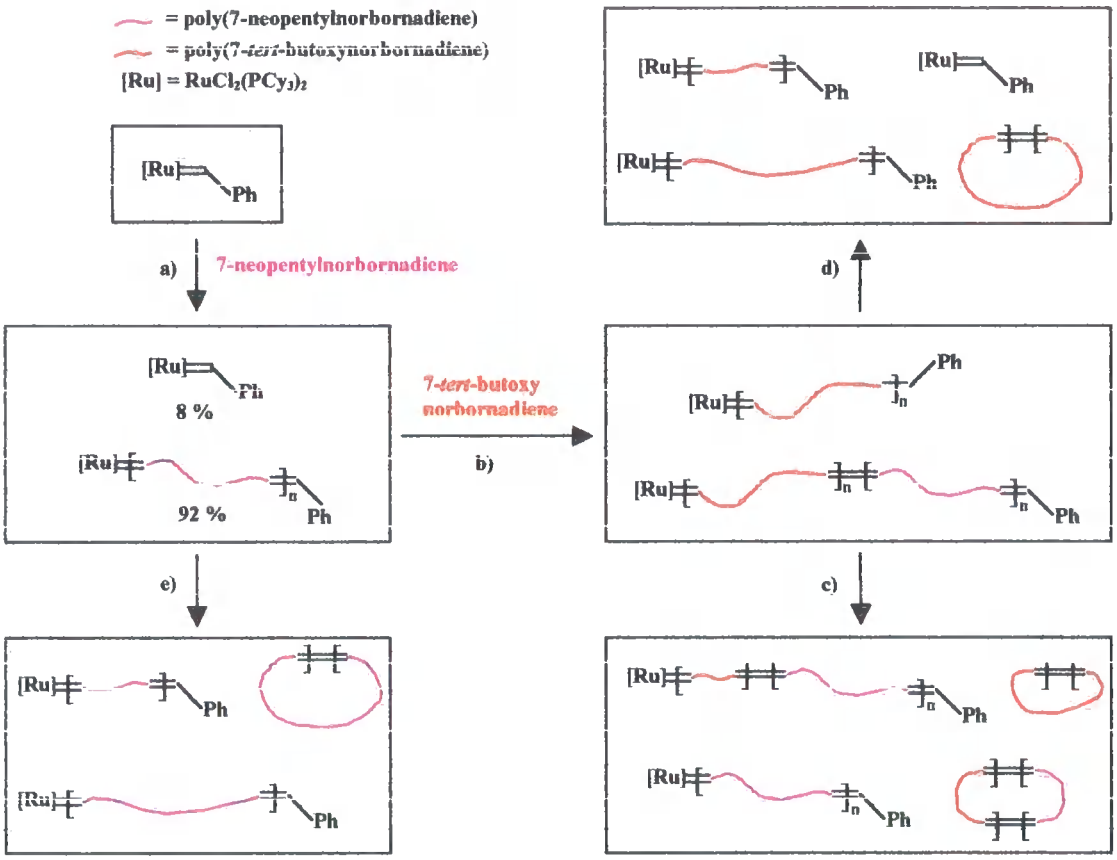

Figure 4.19. Polymer architectures that may arise due to secondary metathesis reactions during a block copolymerisation of monomers ***12a*** *and* ***1***

The observation made in chapter 2, that only 29 % of the initiator is regenerated when initiator **A** mediates the ROMP of monomer **1** using $[M]_o/[I]_o$ = 50, indicates that secondary metathesis reactions do not occur exclusively at the terminal double bonds of the propagating polymer chains, and that backbiting occurs randomly along the propagating polymer backbone.[6] The existence of these backbiting reactions became evident when 7-neopentylnorbornadiene (*Figure 3.1*, **12a**) and monomer **1** were subjected to a block copolymerisation reaction mediated by initiator **A**.

Monomer **12a** (50 equivalents) was added drop wise to initiator **A**, and the polymerisation reached completion in less than 10 minutes, with 92 % of the initiator having been consumed (*Figure 4.19, reaction a*). The alkylidene region of the ^{1}H NMR spectrum exhibited resonances for the alkylidene protons of residual initiator **A** (19.99 ppm) and the propagating poly(**12a**) species (19.21 and 19.05 ppm) (*Figure 4.20a*).

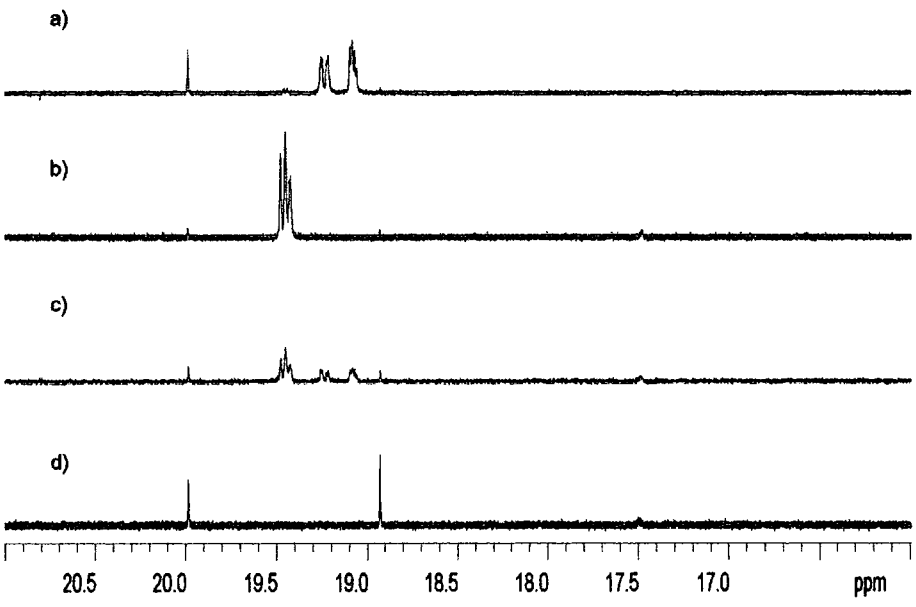

*Figure 4.20. The alkylidene region (21-16 ppm) of 400 MHz ^{1}H NMR spectra ($CDCl_3$) during the blockcopolymerisation of **12a** and **1**. a) initiator **A** and **12a**, b) upon the addition of **1**, c) t = 2.5 hours and d) t = 24 hours*

Upon the addition of 25 equivalents of monomer **1** (*Figure 4.19, route b*), the signals attributed to the alkylidene protons of initiator **A** and poly(**12a**) propagating species immediately disappeared, and characteristic proton resonances of propagating poly (**1**) species (t, 19.36 ppm) emerged (*Figure 4.20b*). Monomer **1** was consumed over a 3 hour period, during which time, resonances attributed to the alkylidene protons of initiator **A**, propagating poly(**12a**) species and species X (~17.5 ppm) gradually appeared at the expense of the propagating poly(**1**) signal at 19.36 ppm (*Figure 4.20c*). The reappearance of the alkylidene proton resonances of propagating poly(**12a**) can only be attributed to the existence of intra- and/or inter-molecular secondary metathesis reactions that take place at internal double bonds along the polymeric backbone of the propagating chains (*Figure 4.19, route c*).

The observed extent of regeneration of the initiator was very low, and was believed to arise from intra- and inter-molecular secondary metathesis reactions involving the small amount of homo-poly(**1**) formed from the reaction between residual initiator **A** (8 %) and monomer **1** (*Figure 4.19, route d*).

It is of interest that the appearance of species X coincided with the onset of regeneration of the initiator when monomer **1** was introduced to the system. This suggests that the presence of oxygen chelation to the ruthenium centre may facilitate the regeneration process.

After 24 hours of reaction, the propagating alkylidene resonances of poly(**12a**) and poly(**1**) had disappeared, and the regenerated initiator **A** and species X remained in solution (*Figure 4.20d*). The additional resonance observed at 18.92 ppm increases in intensity as the reactions proceeds. This resonance may be due to the methylidene species, $RuCl_2(PCy_3)_2(=CH_2)$, which has the same chemical. However the mechanism for its formation in this system is not understood.

4.3.2 Polymer Characterisation using GPC

The existence of secondary metathesis reactions was also evident from analysis of GPC traces of poly(**1**) recovered from the ROMP of monomer **1** mediated by initiator **A** using $[M]_o/[I]_o = 50$. Aliquots of the reaction mixture were taken at frequent intervals during a large scale polymerisation, hence allowing the molecular weight of poly(**1**) to be monitored as a function of time. The aliquots were terminated with ethyl vinyl ether and the recovered polymers analysed by GPC.

Hypothetically, if secondary metathesis reactions only occurred at the propagating polymer chain ends, then the GPC traces should exhibit a bimodal distribution of molecular weights due to cyclic and linear polymers, with molecular weights of approximately 8,200 g/mol and 17,200 g/mol, respectively. It has been determined by ^1H NMR spectroscopy, that the process of regeneration of the initiator takes place over a 24 hour period (See Chapter 2). This indicates that as the reaction proceeds, secondary metathesis reactions are continually occurring, and hence the PDI of the recovered polymer should increase as a function of time. This was not the case. For the first 24 hours of reaction, the GPC traces remained unimodal, the PDI of the

polymer was found to be approximately 2 and the value of M_n fluctuated between 7,500 g/mol and 9,000 g/mol.

A PDI value of 2 indicates that there was a broad distribution of polymer molecular weights in the system, and the fact that the value of M_n remained relatively constant suggests that backbiting reactions occurred randomly along the propagating polymer backbone rather than exclusively at the polymer chain ends. This was confirmed by the GPC trace remaining unimodal as the reaction proceeded.

Although the polydispersity index of the polymers in this system consistently remained ~2, the chromatograms appeared broader than the PDI values suggested. It is established that polymers which have the same molecular weight, but different polymer architectures (e.g. linear, branched or cyclic), elute at different rates due to differences in their hydrodynamic volumes.[10] Hence, a mixture of polymers with different molecular architectures but the same molecular weights give rise to broad GPC traces, even though the polymer is monodisperse. This suggests that poly(**1**) recovered from this system has a distribution of different molecular architectures, and hence it can be tentatively suggested that there are cyclic species present in these samples. However, the absolute value of the molecular weights of the polymers can not be obtained due to the GPC data being calibrated relative to polystyrene standards.

The data obtained from GPC could not be used to conclusively reveal whether regeneration of the initiator was a result of intra- and/or inter-molecular secondary metathesis reactions giving rise to cyclic and/or linear polymers, respectively.

4.3.3 Polymer Characterisation by MALDI-TOF MS

It was anticipated that MALDI-TOF MS would be the ideal analytical tool to determine whether the process of regeneration of the initiator occurred via intra- and/or inter-molecular secondary metathesis reactions at the propagating polymer chain-ends during the polymerisation of monomer **1** mediated by initiator **A.**

The mass of one monomer **1** unit is 164 g/mol. Therefore, upon termination of the polymerisation with ethyl vinyl ether, the molecular weight of cyclic or linear polymer formed from intra- or inter-molecular reactions would be [164n] or [164n+14+90], respectively, where n is the number of monomer units contained

within the poly(**1**) chains, and 14 and 90 are the molecular weights of the chain-ends (*Figure 4.21*).

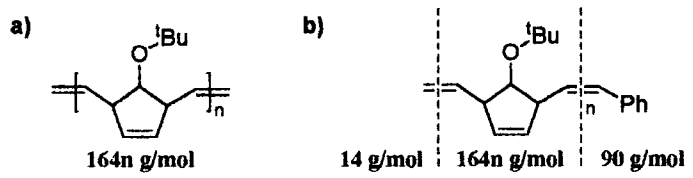

*Figure 4.21. The molecular weight of a) cyclic poly (**1**), and b) ethyl vinyl ether terminated linear poly(**1**)*

The application of GPC for characterisation of polymeric materials provides an average molecular weight distribution of a sample, whereas MALDI-TOF MS, being an extremely sensitive technique, allows determination of the precise molecular weight of polymer architectures contained within a sample. Therefore, upon subjecting the recovered polymer samples to MALDI-TOF MS, the linear polymers should be spaced 104 g/mol from the cyclic polymers, hence making it possible to clearly determine whether intra- or inter-molecular reactions, or both, are responsible for regeneration of the initiator.

Unfortunately, poly(**1**) samples could not be characterised by MALDI-TOF MS due to the samples being insufficiently ionised for them to be successfully projected through the spectrometer.

The polymer obtained from the ROMP of *exo*-N-phenyl-5,6-dicarboxyimidonorbornene (*Figure 2.2*, **3a**) has been previously characterised by MALDI-TOF MS.[11] In order to overcome the problems associated with MALDI-TOF MS of poly(**1**), the synthesis of *exo*-N-phenyl-5,6-dicarboxyimido-7-*tert*-butoxynorbornene (*Figure 4.22*) which incorporates the functionalities of both monomer **1** and *exo*-N-phenyl-5,6-dicarboxyimidonorbornene (**3a**) was attempted. The resulting ROMP polymer should be suitable for MALDI-TOF MS characterisation due to the presence of the *exo*-N-phenyl-5,6-pendant groups, and regeneration of the initiator should be observed due to 7-alkoxy substituents contained within the polymer backbone. In attempts to prepare *exo*-N-phenyl-5,6-dicarboxyimido-7-*tert*-butoxynorbornene two synthetic routes were tried (*Figure 4.22*), both of which were unsuccessful.

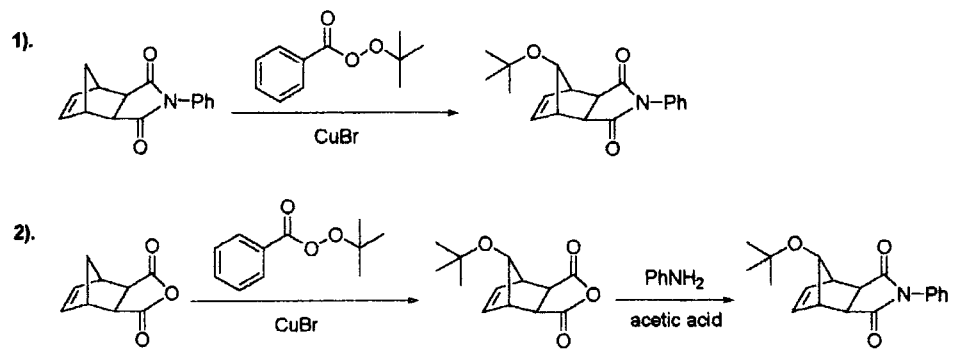

Figure 4.22. The two synthetic routes attempted for the preparation of exo-N-phenyl-5,6-dicarboxyimido-7-tert-butoxynorbornene

An additional method for distinguishing between the two mechanisms by which regeneration of the initiator occurs, would be to perform the ROMP of monomer **1** mediated by initiator **A** at variable concentrations. Presumably, a reduction in the concentration of propagating polymer chains, would favour intramolecular secondary metathesis reactions over intermolecular secondary metathesis reactions and hence increase the amount of cyclic polymer relative to linear polymer. However, these types of reactions were not performed due to being unable to find a suitable characterisation method for the resultant polymer samples.

4.4 The Effect of Oxygen Chelation to the Ruthenium Centre on the Process of Regeneration of the Initiator

So far in this chapter, evidence has been provided for the existence of both secondary metathesis reactions and oxygen chelation to the ruthenium centre when monomer **1** is subjected to ROMP mediated by initiator **A**. It was previously proposed that in this system, chelation of oxygen to the metal centre may facilitate the process of regeneration by enhancing the occurrence of secondary metathesis reactions at the propagating polymer chain-ends. This section explores in further detail the correlation between oxygen chelation to the ruthenium centre and the regeneration process, and also the role that pendant 7-*tert*-butoxy groups play in this process when monomer **1** is subjected to ROMP mediated by initiator **A**.

4.4.1 Evidence of Oxygen Chelation to the Ruthenium Centre

The nature of the propagating species that arise when oxygen-containing monomers, derived from norbornene and norbornadiene, are subjected to ROMP mediated by

initiator **A** has been elucidated by addition of either excess PCy_3 or CuCl. The nature of the oxygen-chelated propagating species that are observed in the reactions of 7-alkoxynorbornadiene monomers are qualitatively different to those observed using monomers where the oxygen is attached to pendant groups in the 5 and/or 6 positions of norbornene. In the former case, the peak due to the oxygen-chelated ruthenium alkylidene species (*Figure 4.14*, structure **IIb**) appears at a relatively low frequency in the proton NMR spectrum (~ 17.5 ppm) and grows in intensity after all the monomer present has reacted. In the latter case the corresponding signals (*Figure 4.7*, structure **VIIb**) are typically higher in frequency (between 19.0 and 18.5 ppm), and are present to a significant extent before all the monomer has been consumed. The additional signals are much more readily apparent in the latter case if the monomer contains carbonyl groups rather than, for example, ethers. The interpretation of these observations is that the oxygen atom from the polymer backbone coordinates to the ruthenium centre in place of one of the PCy_3 ligands. In the former case this chelation is from the oxygen on the monomer unit immediately adjacent to the ruthenium centre via a 5-membered ring to give a species which is structurally similar to that found in initiator **F**, while in the latter case the chelation can be from any oxygen along the polymer backbone.

In the case of the 7-alkoxy substituents, the fact that the additional signal at ~17.5 ppm was largely absent until all the monomer had been consumed is significant. Molecular models revealed that chelation of oxygen from the monomer unit immediately adjacent to the ruthenium centre can only arise if the double bond which was *syn* to the 7-alkoxy substituent in the monomer is opened (*Figure 4.23*).

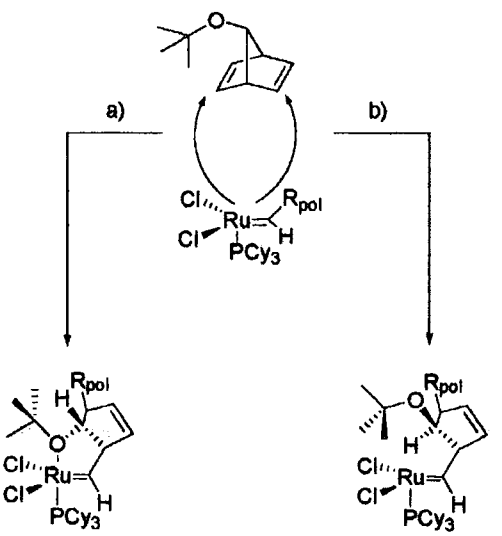

*Figure 4.23. Insertion of **1** into propagating ruthenium alkylidene species by, a) syn, or b) anti enchainment*

It is established, from ^{13}C NMR spectroscopy, that the polymerisation of monomer **1** mediated by initiator **A** proceeds predominantly by opening the double bond which is *anti* to the alkoxy substituent ($\sigma_s < 0.07$ between 6 and 10 hours after mixing).[8] When monomer **1** is polymerised using the Schrock complexes, Mo(=CHCMe$_2$Ph)(=NC$_6$H$_3$-2,6-*i*-Pr$_2$)(OCMe(CF$_3$)$_2$)$_2$ or Mo(=CHCMe$_2$Ph)(=NC$_6$H$_3$-2,6-*i*-Pr$_2$)(OCMe$_3$)$_2$, significantly more *syn* enchainment is observed (σ_s = 0.47 and σ_s = 0.34, respectively). In these cases it was concluded that *syn* enchainment involved complexation of oxygen to the metal centre via a 5-membered ring, and evidence to support this was obtained from Nuclear Overhauser Experiments (nOe).[8] For the ROMP of monomer **1** mediated by initiator **A**, it was not possible to observe conclusive nOe evidence that the signal at ~17.5 ppm in ^1H NMR spectra arises from *syn* enchainment. However, it is known that the geometry associated with ruthenium complexes containing oxygen chelation via a 5-membered ring leads to a significant coupling between the ruthenium-alkylidene proton and the phosphine ligand, which is not otherwise observed (Section 3.2). The alkylidene proton resonance of initiator **F** appears as a doublet ($^3J_{P\text{-}H}$ = 4.4 Hz), whereas for initiator **A** no coupling of the alkylidene proton is observed. The presence of coupling is not immediately apparent on the signal at ~17.5 ppm, but it is noteworthy that the linewidth of the resonance is greater than the expected coupling, which would therefore mask the coupling. Again, this matter could not be probed using 2D correlation NMR experiments, so instead it was investigated using selective ^{31}P decoupling. It was shown that by selectively decoupling the ^{31}P signal at 54.4 ppm (*Figure 4.24*) the linewidth of the proton signal at ~17.5 ppm narrowed from 12 Hz to 9 Hz, thereby confirming the presence of the coupling. Selective ^{31}P decoupling of other resonances, results in no change in linewidth of any alkylidene resonances in ^1H NMR spectra, indicating that the other propagating species (19.36 ppm, triplet) has a geometry consistent with bis(phosphine) propagating species similar in structure to initiator **A** (*Figure 4.25a*).

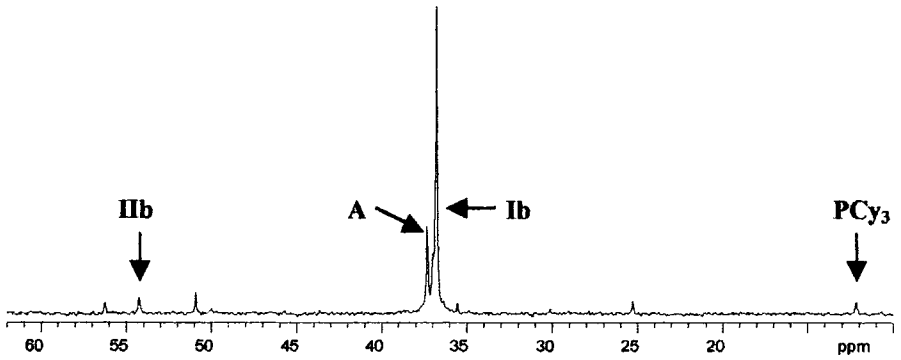

*Figure 4.24. The 202 MHz ^{31}P NMR spectra ($CDCl_3$) when the ROMP of **1** is mediated by initiator **A**. $[M]_o/[I]_o=50$*

The appearance of the mono(phosphine) oxygen-chelated ruthenium alkylidene species **IIb** at 54.4 ppm in ^{31}P NMR spectra is consistent with the chemical shift of the phosphorus resonance of initiator **F** observed at 59.8 ppm which has an analogous structure (*Figure 4.25b*). It is also apparent that during the ROMP of monomer **1** mediated by initiator **A** a resonance of almost equal intensity to **IIb** is seen at 12.2 ppm in the ^{31}P NMR spectra, which corresponds to a stoichiometric amount of free PCy_3 (*Figure 4.24*).

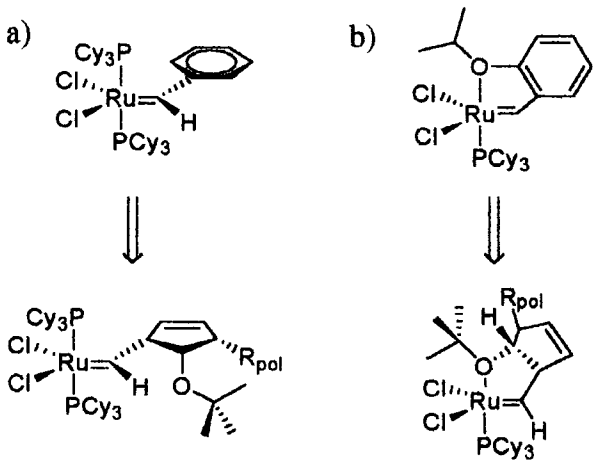

*Figure 4.25. Comparison of the geometries of alkylidene protons of a) initiator **A** and anti-inserted monomer **1** units, and b) initiator **F** and syn-inserted monomer **1** units*

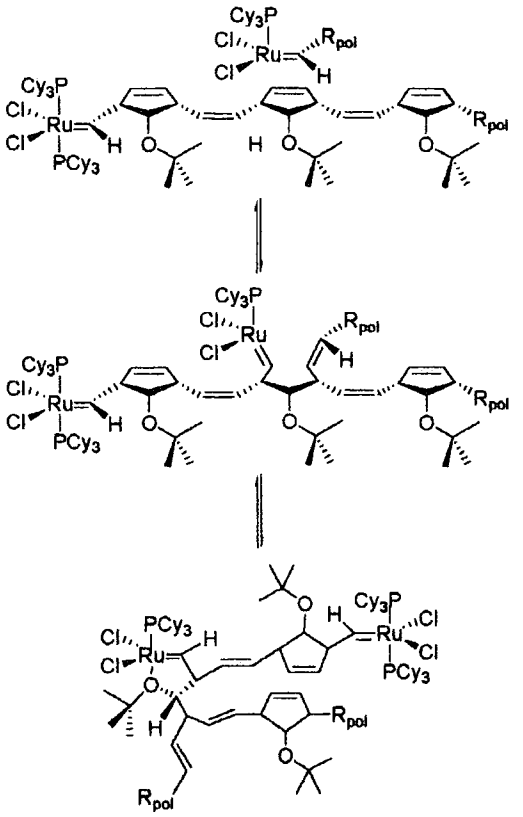

Figure 4.26. The intermolecular secondary metathesis reaction that may occur the monomer has been consumed when monomer 1 is subjected to ROMP by initiator A, giving rise to chain branching

The observation that the signal at ~17.5 ppm grows in intensity after all the monomer has been consumed when monomer **1** is subjected to ROMP by initiator **A** indicates that it arises because once the initiator has polymerised all the monomer, via *anti* enchainment, it goes on to react with the double bonds which were *syn* in the monomer and now contained within the cyclopentenyl rings of the polymer backbone (*Figure 4.26*). The orientation of the alkoxy oxygen atom is now such that it is possible for it to chelate to the ruthenium centre. These secondary metathesis reactions result in the formation of cyclic polymers if they are intramolecular, or chain branching if they are intermolecular.

Interestingly, ^{13}C NMR analysis of the polymer formed when monomer **1** is subjected to ROMP by initiator **F** revealed that the polymerisation proceeds predominately by *anti* enchainment. Therefore, it is possible that the low intensity broad signal at 17.5 ppm in this system is in fact a dormant alkylidene species which arises due to *syn*

enchainment, and that the active *anti*-inserted propagating species are not observable on the NMR timescale.[12]

Regeneration of the initiator occurs as a result of secondary metathesis reactions which take place at the chain-ends. Interpretation of the spectroscopic data provided in this section, reveals that oxygen chelation to ruthenium centre when monomer **1** is subjected to ROMP mediated by initiator **A**, is from the adjacent monomer unit of the propagating polymer chain rather than a terminal unit, which it was proposed would facilitate the regeneration process (*Figure 2.15*). However, it is significant that regeneration of the initiator is only observed in systems where this type of adjacent oxygen chelation to the ruthenium centre is apparent, and this is limited to systems in which the ROMP of 7-alkoxynorbornadienes is mediated by initiator **A**. Therefore, it is possible that these two occurrences are part of one and the same process. The 7-alkoxy functionality of the monomer appears to somehow activate the terminal double bond of the propagating polymer chain which enables it to undergo secondary metathesis with the ruthenium alkylidene and hence induce regeneration. This phenomenon is not otherwise observed in any ROMP system mediated by initiator **A**, and this highlights that it is specifically the presence of an alkoxy group in the 7-position which facilitates the regeneration process.

4.4.2 The Effects of Added Phosphines Prior to Initiation of ROMP

It was proposed that oxygen chelation to a ruthenium centre from monomer units at the chain-end of propagating polymers would facilitate the regeneration process (*Figure 2.15*). However, the previous section reports that in fact it is oxygen from the adjacent monomer units rather than terminal ones which chelate to the ruthenium centre during the ROMP of monomer **1** mediated by initiator **A**.

In order to assess whether chelation of oxygen from the propagating polymer backbone to the ruthenium centre (i.e. formation of propagating species **IIb**) does promote the process of regeneration of the initiator in this system, various amounts of PCy_3 were added to initiator **A** before it was used to mediate the ROMP of monomer **1**.

The chelating oxygen atom in species of the type **IIb** can be displaced by the addition of PCy_3 (Section 4.2.6). Therefore, addition of PCy_3 to initiator **A** before the start of

the polymerisation of monomer **1**, should retard the formation of **IIb**, and hence reduce the extent of regeneration of the initiator observed.

*Table 4.2. Results from the ROMP of monomer **1** mediated by initiator **A** with various amounts of PCy_3 added prior to initiation*

PCy_3	Monomer consumption / hrs	Initiator consumption / hrs [a]	Regeneration time period / hrs [b]	Extent of regeneration / %	Species **VII** present [c] / %
0	1	0.25	10	22	13
0.1	1.25	0.25	23	22	9
0.25	2.5	0.8	35	19	9
0.5	8	2.25	48	20	4
0.75	12	4.75	50	16	2
1	22	6	125	12	2
2	30	23	125	8	< 1
5	100	30	150	8	-

[a] In all cases > 95 % of initiator was consumed. [b] Based on the time it takes for the maximum extent of regeneration of the initiator to be observed. [c] Highest observed value relative to total intensity of alkylidene resonances in first ^1H NMR spectrum.

A series of experiments were performed in which varying amounts of PCy_3 (0, 0.1, 0.25, 0.5, 0.75, 1, 2 and 5 equivalents) were added to initiator **A** before it mediated the ROMP of monomer **1**. The polymerisations were monitored by ^1H NMR spectroscopy.

As the concentration of added PCy_3 was increased, the rate at which all aspects of the polymerisation process took place was retarded (*Table 4.2*). This was attributed to increased levels of PCy_3 resulting in a decrease in concentration of active mono(phosphine) propagating ruthenium centres relative to dormant bis(phosphine) alkylidene, hence impeding the rate at which olefin metathesis reactions occurred.[3] This was reflected by an increase in concentration of PCy_3 resulting in a decrease in the rate of consumption of the monomer and the initiator, and an extension of the time period over which regeneration of the initiator was observed. This was evident from the ^1H NMR spectra obtained for each system after 2 hours of reaction (*Figure 4.27*).

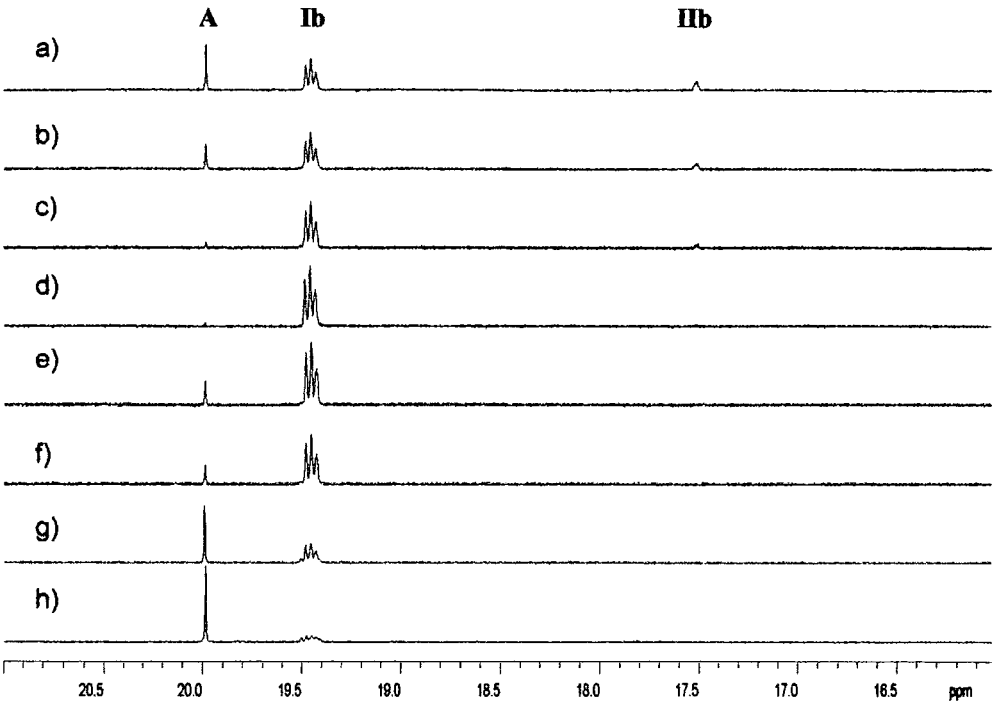

Figure 4.27. The alkylidene region of 500 MHz ^{1}H NMR spectra ($CDCl_3$) obtained 2 hours after the initiation of the ROMP of ***1*** *by initiator* ***A*** *with a) 0, b) 0.1, c) 0.25, d) 0.5, e) 0.75, f) 1, g) 2, and h) 5 equivalents of PCy_3 added 10 minutes prior to initiation. $[M]_o/[I]_o=50$, $[I]_o=15$ mM*

In systems a-c (*Figure 4.27a-c*), after 2 hours of reaction, the initiator had been completely consumed and was in the process of being regenerated at the expense of the propagating species **Ib**. The rate at which regeneration of the initiator occurred was found to decrease as the concentration of PCy_3 was increased. In systems d-f, the initiator was still being consumed by residual monomer after 2 hours of reaction, and the alkylidene proton resonances of propagating species **Ib** were still increasing in intensity. The amount of unreacted initiator that remained after 2 hours of reaction was more pronounced in systems where the concentration of added PCy_3 was greater (g-h).

The results quoted in *Table 4.2* imply that as the level of PCy_3 in the system was increased, the extent of regeneration of the initiator decreased accordingly. However, it is worth considering that this may not be a realistic reflection of the amount of initiator that was genuinely regenerated in the systems. In systems where monomer consumption was very slow, it is possible that regenerated initiator was subsequently consumed by the remaining monomer and hence the observed extent of regenerated

initiator was lower than the actual extent of regenerated initiator. Nevertheless, the reduction in the extent of regeneration of the initiator coincided with a reduction in the amount of mono(phosphine) propagating species **IIb** that was observed as the concentration of PCy_3 in the system increased (*Table 4.2*). The system in which the highest intensity of mono(phosphine) species **IIb** was observed was when no PCy_3 was added prior to initiation. With an increased concentration of PCy_3, the observed intensity of **IIb** decreased accordingly, to the extent that when 5 equivalents of PCy_3 were added, the signals for **IIb** were undetectable by ^1H NMR spectroscopy (*Figure 4.27h*).

The observed reduction in the extent of regeneration of the initiator coincided with a reduction in the amount of mono(phosphine) species **IIb** present. This indicates that the formation of **IIb** may somehow facilitate the process of regeneration of the initiator when monomer **1** is subjected to ROMP mediated by initiator **A**.

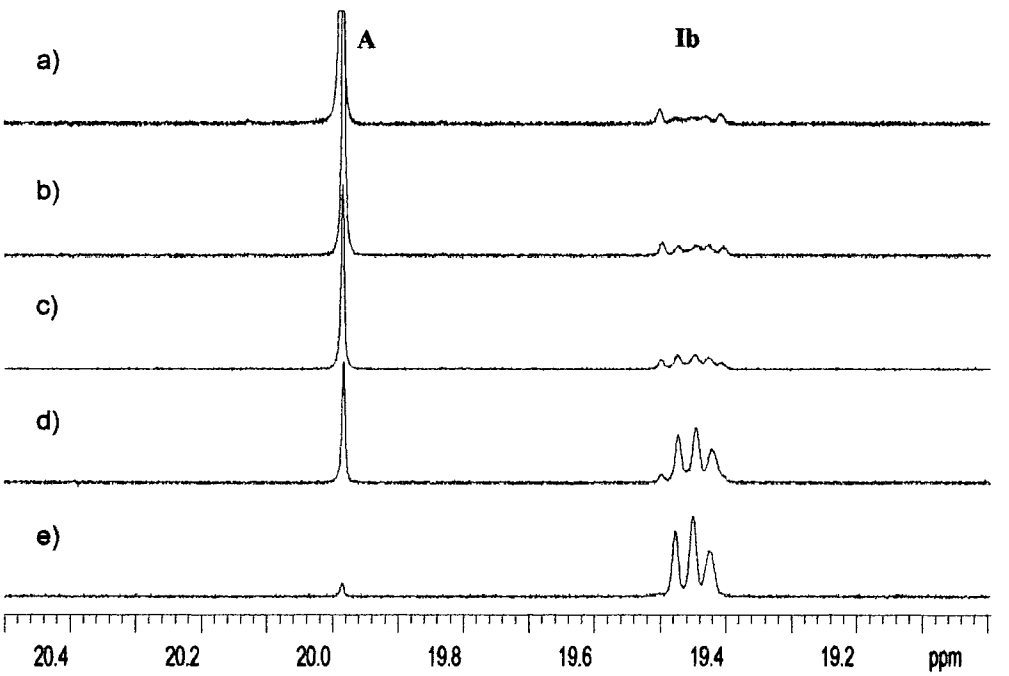

*Figure 4.28. The alkylidene region of 500 MHz ^1H NMR spectra ($CDCl_3$) after a) 0.5, b) 1, c) 2, d) 6 and e) 24 hours of reaction when **1** is subjected to ROMP mediated by initiator **A** with 5 equivalents of PCy_3 added 10 minutes prior to initiation. $[M]_o/[I]_o=50$, $[I]_o=15$ mM*

An additional point of interest was the appearance of the bis(phosphine) propagating species **Ib** in the ^{1}H NMR spectra during the early stages of the polymerisation. In the absence of PCy_3, the signal attributed to propagating species **Ib** exhibited the simple form of a triplet throughout the entire reaction. However, with added PCy_3, the propagating species **Ib** appeared in ^{1}H NMR spectra with different multiplicities. *Figure 4.28* shows the appearance of species **Ib** at various stages of the polymerisation when 5 equivalents of PCy_3 were added to the initiator before the start of the reaction.

After 30 minutes of reaction, when only a fraction of the monomer and initiator had been consumed, the resonances attributed to the propagating species **Ib** were complex, and peaks were seen either side of the low intensity characteristic triplet (*Figure 4.28a*). These two signals are attributed to the alkylidene protons of propagating polymer chains which contain only one (or a few) monomer units. As the polymerisation proceeded (*Figure 4.28a-e*) and more monomer and initiator were consumed, the intensity of these two signals diminished as the characteristic triplet emerged from the baseline. This corresponds to the number of monomer units in each propagating polymer chain increasing and hence giving rise to propagating ruthenium alkylidene species which have similar environments. After 24 hours of reaction, the triplet was very pronounced (*Figure 4.28e*).

4.4.3 The Effects of Added Phosphines after Complete Monomer Consumption

In order to monitor the affect that PCy_3 has on the process of regeneration of the initiator and the appearance of the alkylidene resonances in the ^{1}H NMR spectra once all the monomer has been consumed, a complimentary set of experiments similar to those described in Section 4.4.2 were performed. The ROMP of monomer **1** was mediated by initiator **A**, using $[M]_o/[I]_o = 50$, and after 30 minutes of reaction, when > 95% of monomer had been consumed, varying amounts of PCy_3 (0, 0.1, 0.25, 0.5, 0.75 and 1 equivalents) were added.

Due to the process of regeneration occurring in the early stages of the polymerisation, regenerated initiator was observed in all of the systems (*Figure 4.29a-f*). Upon the addition of PCy_3, the extent of subsequent regeneration of initiator was found to decrease with an increase in concentration of PCy_3 (*Table 4.3*). In the case of 0.75

and 1 added equivalents of PCy_3, less than 1% of subsequent regeneration was observed.

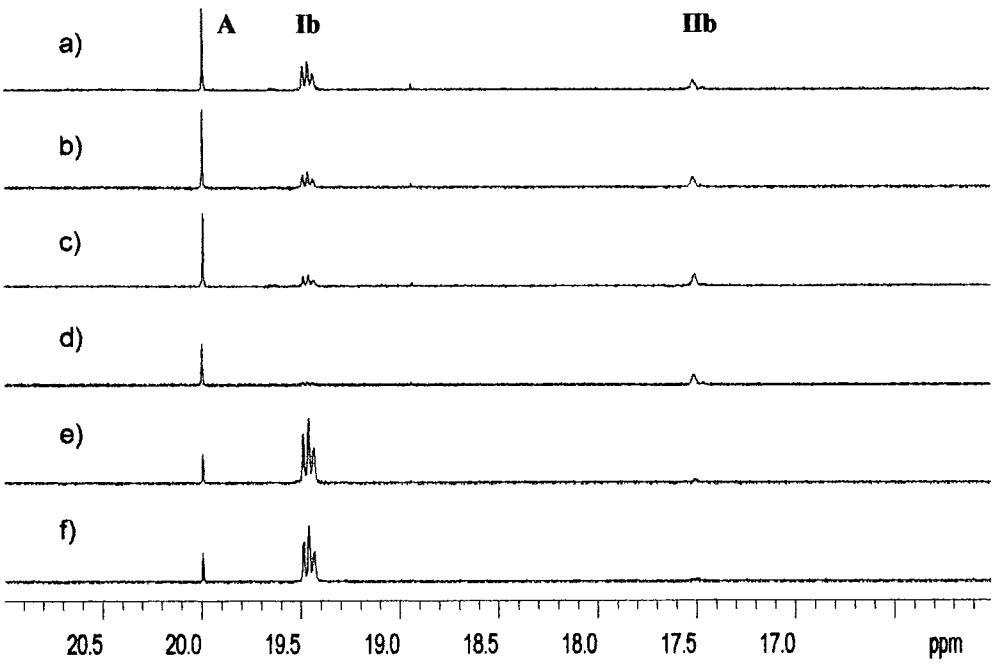

*Figure 4.29. The alkylidene region of 500 MHz ^1H NMR spectra ($CDCl_3$) obtained after 6 hours of reaction when the ROMP of **1** is mediated by initiator **A**, with a) 0, b) 0.1, c) 0.25, d) 0.5, e) 0.75 and f) 1 equivalents of PCy_3 added after the monomer is consumed. $[M]_o/[I]_o=50$, $[I]_o=15$ mM*

*Table 4.3. The extent of regeneration observed when PCy_3 is added to the ROMP of **1** mediated by initiator **A** after complete consumption of the monomer*

System	Added PCy_3	Extent of regeneration of initiator [a] / %
a	0	17
b	0.1	7
c	0.25	6
d	0.5	3
e	0.75	< 1
f	1.00	< 1

[a] Based on increasing intensity of initiator resonance after addition of PCy_3.

The alkylidene proton resonances for the propagating species **IIb** were seen in all of the systems (~17.5 ppm) and their intensity decreased as the concentration of added PCy_3 was increased (*Figure 4.29*). This was due to excess PCy_3 preventing oxygen chelating to the ruthenium centre. The formation of the mono(phosphine) propagating species **IIb** is believed to somehow facilitate the process of regeneration. The fact that a lower concentration of mono(phosphine) propagating species **IIb** coincided with a reduction in the extent of regeneration of the initiator observed, supports this hypothesis.

In theory, the presence of free PCy_3 in a ROMP system mediated by initiator **A** should enhance the stability of bis(phosphine) propagating alkylidene species, due to the fact that ruthenium alkylidene species of this type decompose via the coupling of two mono(phosphine) species to form unstable bimetallic ruthenium complexes.[13] In the case of 0.75 and 1 equivalents of added PCy_3, this was found to be the case and the intensity of the bis(phosphine) propagating species **Ib** were found to remain almost constant after 24 hours of reaction. However, when 0, 0.1, 0.25 or 0.5 equivalents of PCy_3 were added to the polymerisation, the rate of decomposition of propagating species **Ib** was found to be accelerated by an increase in concentration of PCy_3. The reason for this behaviour is not understood.

A small resonance was observed in the ^1H NMR spectra at 18.92 ppm in systems a-d after 6 hours of reaction (*Figure 4.29*). This chemical shift is consistent with that of the methylidene species, $RuCl_2(PCy_3)_2(=CH_2)$. However, the mechanism for its formation is not known.

4.5 Summary

The observation of regeneration of the initiator during ROMP reactions mediated by initiator **A** is exclusive to bicyclic olefin monomers which contain oxygen-functionalised pendant groups in the 7-position. Regeneration occurs via secondary metathesis reactions at the propagating polymer chain-ends either intra- or inter-molecularly.

It has been established that not all secondary metathesis reactions result in regeneration of the initiator, and there are nine possible ways in which the ruthenium alkylidene can react with double bonds (internal or terminal) along the propagating

polymer backbone. The block copolymerisation of monomer **12a** and monomer **1** mediated by initiator **A** confirms that backbiting reactions occur along the entire polymer backbone. Secondary metathesis reactions at the polymer chain-ends which are believed to result in regeneration of the initiator are only apparent when oxygen is introduced in the 7-position of the monomer and hence in the propagating polymer backbone. The onset of regeneration coincides with the presence of oxygen chelation to the ruthenium centre.

GPC traces of poly(**1**) recovered from ROMP mediated by initiator **A** appear broad, whereas the polydispersity of the polymer remains relatively narrow. The absolute value of the molecular weights of the polymers could not be obtained due to the GPC data being calibrated relative to polystyrene standards, but the PDI of the polymer remained unimodal and M_n fluctuated between 7,500 and 9,000 g/mol. The data obtained from GPC did not conclusively reveal whether the process of regeneration of the initiator resulted in the formation of cyclic or linear polymeric materials.

MALDI-TOF MS could not be used to confirm the types of polymer architectures present in the poly(**1**) samples, due to insufficient ionisation preventing successful projection of the polymer through the spectrometer. Attempts to prepare modified monomers, of which the resulting polymers would be more suited to characterisation by MALDI-TOF MS, were also unsuccessful.

ROMP reactions of bicyclic olefin monomers mediated by initiator **A** were performed, and the identity of the propagating alkylidene species that arise have been unambiguously identified using ^{1}H NMR spectroscopy. In all of the systems studied, bis(phosphine) propagating species were observed, and their identity was confirmed by their disappearance upon the addition of CuCl (a phosphine sponge) to the system. In the case of non-oxygen-containing monomers, this was the only type of propagating species observed. When bicyclic olefin monomers containing oxygen were subjected to ROMP mediated by initiator **A**, additional propagating alkylidene signals were apparent and their specific chemical shift and multiplicity was found to be dependant on the position and nature of the oxygen-containing functionality. These resonances are attributed to mono(phosphine) alkylidene species in which oxygen from the propagating polymer backbone chelates to the ruthenium centre. These species remained in solution upon the addition of CuCl indicating that the

ruthenium centre does not possess labile phosphine ligands, but they disappeared in the presence of excess free PCy_3, due to displacement of the chelating oxygen atom.

The relationship between the process of regeneration of the initiator and chelation of oxygen from the propagating polymer backbone to the ruthenium centre has been probed. Molecular modeling revealed that oxygen chelation to the ruthenium centre when monomer **1** is subjected to ROMP mediated by initiator **A**, is from the adjacent monomer unit of the propagating polymer chain rather than a terminal unit, which it was proposed would facilitate the regeneration process. However, it is significant that regeneration of the initiator is only observed in systems where this type of adjacent oxygen chelation to the ruthenium centre is apparent, and this is limited to systems in which the ROMP of 7-alkoxynorbornadienes is mediated by initiator **A**. Therefore, it is possible that these two occurrences are part of one and the same process. This phenomenon is supported by the observation that oxygen chelation to the ruthenium centre is prevented by the addition of PCy_3, and that an increase in concentration of PCy_3 coincides with a reduction in the extent of regeneration of the initiator observed. Addition of PCy_3 is also found to retard all aspects of the polymerisation process.

4.6 References

1. C. Slugovc, S. Demel, S. Riegler, J. Hobisch, F. Stelzer, *Macromolecular Rapid Communications* **2004**, *25*, 475.
2. S. Demel, W. Schoefberger, C. Slugovc, F. Stelzer, *Journal of Molecular Catalysis A: Chemical* **2003**, *200*, 11.
3. C. W. Bielawski, R. H. Grubbs, *Macromolecules* **2001**, *34*, 8838.
4. B. R. Maughon, R. H. Grubbs, *Macromolecules* **1997**, *30*, 3459.
5. W. Buchowicz, M. N. Holerca, P. Percec, *Macromolecules* **2001**, *34*, 3842.
6. D. M. Haigh, A. M. Kenwright, E. Khosravi, *Tetrahedron* **2004**, *60*, 7217.
7. K. J. Ivin, A. M. Kenwright, E. Khosravi, *Chemical Communications* **1999**, 1209.
8. K. J. Ivin, A. M. Kenwright, E. Khosravi, J. G. Hamilton, *Macromolecular Chemistry and Physics* **2001**, *202*, 3624.
9. E. L. Dias, S. T. Nguyen, R. H. Grubbs, *Journal of the American Chemical Society* **1997**, *119*, 3887.

10. C. W. Bielawski, D. Benitez, R. H. Grubbs, *Journal of the American Chemical Society* **2003**, *125*, 8424.

11. T. C. Castle, *Ph.D. Thesis (University of Durham)* **2004**.

12. J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus, Jr., A. H. Hoveyda, *Journal of the American Chemical Society* **1999**, *121*, 791.

13. M. Ulman, R. H. Grubbs, *Journal of Organic Chemistry* **1999**, *64*, 7202.

Chapter 5

Induced Regeneration of Well-Defined Ruthenium Complexes from Olefin Metathesis Reactions Mediated by Initiator A

5.1 Introduction

This chapter focuses on the development of a technique which allows metathesis catalysts to be recovered from ROMP systems mediated by $RuCl_2(PCy_3)_2(=CHPh)$ (*Figure 2.1*, **A**) upon the addition of appropriate terminating agents once the polymerisation reaches completion. The methodology is also applied to Ring-Closing Metathesis (RCM) reactions mediated by initiator **A**.

Attention is paid to the possible orientations in which terminating agents can insert into ruthenium alkylidene bonds via [2+2] cyclo-addition reactions. This, coupled with careful consideration of the mechanism by which auto-regeneration of the initiator occurs when 7-alkoxynorbornadiene monomers are subjected to ROMP mediated by initiator **A**, aids the choice of appropriate terminating agents that successfully induce the formation of ruthenium complexes from ROMP systems.[1]

The use of initiator **A** to mediate ROMP reactions allows the preparation of polymers with controlled molecular architectures and permits the incorporation of high degrees of functionality.[2-5] It is also used extensively in the field of Ring-Closing Metathesis (RCM).[6-11] Despite this, the use of initiator **A**, and related complexes, on an industrial scale is limited by their high cost and the fact that they are unrecoverable once the reaction reaches completion. Financially, this new method of inducing the formation of metathesis complexes from olefin metathesis reactions mediated by initiator **A** by the simple addition of a terminating agent once the reaction is finished is very attractive. An expensive non-recyclable metal initiator is turned into a cost effective re-usable initiator.

It is envisaged that, if active metathesis complexes can be easily recovered from ROMP systems mediated by initiator **A** and used in subsequent olefin metathesis reactions, then the development of continuous rather than batch processing should be achievable. The advent of supported initiators should facilitate this development.[12]

5.2 Cross Metathesis between Initiator A and Acyclic Olefins

As discussed in section 2.2, ROMP reactions are considered to be living. In order to quench a ROMP reaction a terminating agent needs to be introduced to the system. This leads to the deactivation of the active propagating ruthenium alkylidene species, and cleavage of the polymer from the ruthenium centre. When ethyl vinyl ether is

used as a terminating agent for ROMP mediated by initiator **A** the exclusive formation of $RuCl_2(PCy_3)_2(=CHOEt)$ is seen, and no $RuCl_2(PCy_3)_2(=CH_2)$ is observed (*Figures 2.8 and 2.9*). In order to understand the selective nature of the cross-metathesis (CM) reaction that occurs upon the addition of ethyl vinyl ether to ROMP reactions, the steric interactions that arise when propagating ruthenium species and acyclic olefins undergo [2+2] cyclo-addition reactions need to be considered.

It is established that the rate at which metallacyclobutanes are formed, when acyclic olefins are added to initiator **A**, is dependant on steric interactions between the ruthenium alkylidene and the terminal olefin.[2] The terminal olefin can insert into the ruthenium-carbon double bond in two different orientations giving rise to distinctly different metallacyclobutane species (*Figure 5.1*). The formation of intermediate α is favoured over β due to the substituents (Ph and R) being in the 1,3 position, hence reducing their steric interaction. This route leads to the formation of the kinetic product, a substituted alkylidene complex.

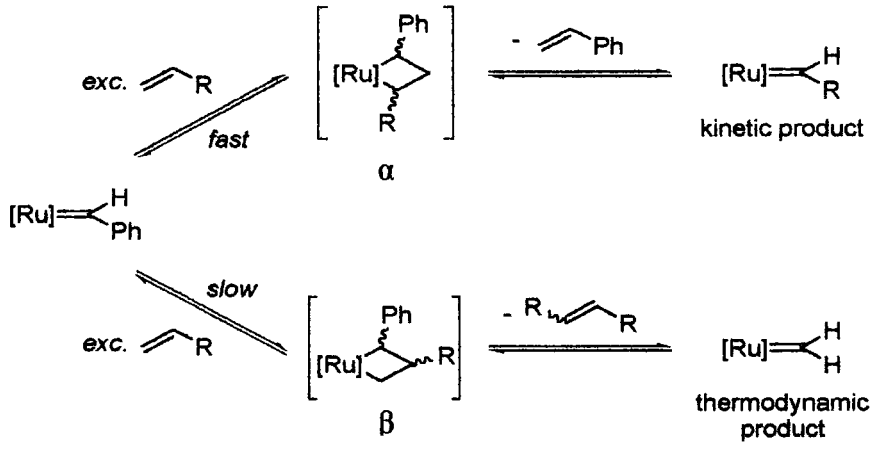

*Figure 5.1. The formation of kinetic and thermodynamic products when terminal olefins react with initiator **A**, via intermediates α and β, respectively*

The rate of formation of intermediate α is dependent on the steric bulk of the incoming acyclic terminal olefin and its interaction with the metal moiety. In the case of linear olefins (R = Me, Et, ^{n}Bu) the reaction proceeds very quickly, but increased substitution at the neighbouring carbon impedes the [2+2] cyclo-addition reaction. In the case of 3-methylbut-1ene (R = ^{i}Pr) the metallacyclobutane forms very slowly and for 3,3-dimethylbut-1-ene (R = ^{t}Bu) no reaction is observed (*Figure 5.2*). If the substituted alkylidene complexes are not immediately isolated, then they undergo

slow reaction with excess olefin. This results in the formation of the methylidene complex, $RuCl_2(PCy_3)_2(=CH_2)$, the thermodynamic product.

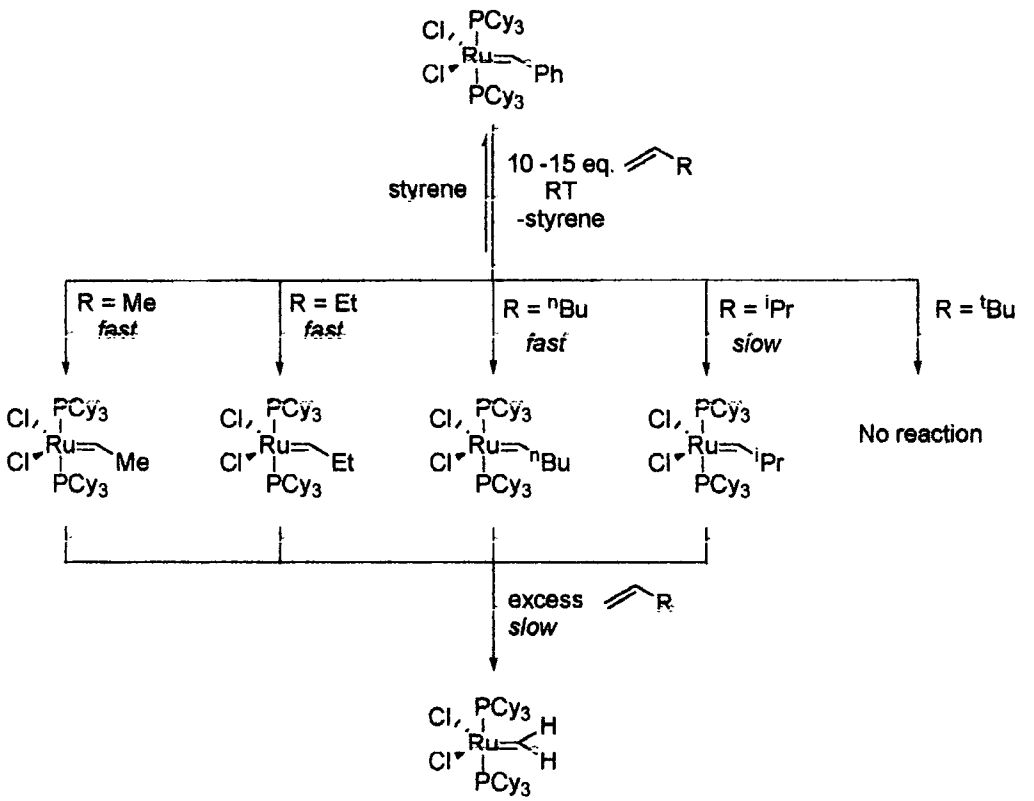

Figure 5.2. CM between terminal acyclic olefins and initiator A

The addition of symmetrical disubstituted olefins (2-butene, 3-hexene) to initiator **A** results in substituted alkylidene complexes, but the rate of their formation is retarded (relative to reaction with monosubstituted olefins) due to the presence of three substituents in the metallacyclobutane intermediate, γ (*Figure 5.3*). The use of disubstituted olefins as CM substrates eliminates the formation of the thermodynamic product $[RuCl_2(PCy_3)_2(=CH_2)]$ due to the absence of terminal double bonds.

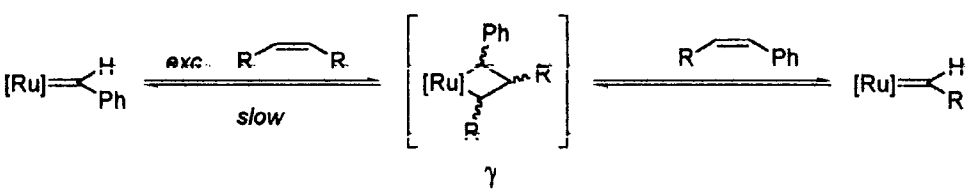

Figure 5.3. CM between symmetrical disubstituted acyclic olefins and initiator A

When an excess of ethyl vinyl ether is added to initiator **A**, the kinetic product is $RuCl_2(PCy_3)_2(=CHOEt)$ (14.58 ppm), and based on the rationale described above, this

is expected. However, after 48 hours of reaction there is no evidence for formation of the thermodynamic methylidene product, and $RuCl_2(PCy_3)_2(=CHOEt)$ is still the only alkylidene complex observed by ^1H NMR spectroscopy. It is possible that the formation of the thermodynamic methylidene species is not permitted due to the oxygen atom of the approaching olefin chelating to the ruthenium centre and hence orientating the double bond in a manner which dictates that subsequent CM reactions result in the formation of $RuCl_2(PCy_3)_2(=CHOEt)$ (*Figure 5.4*).

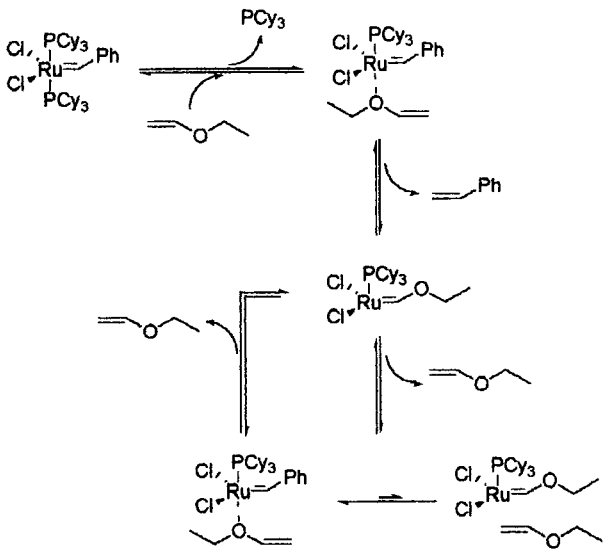

*Figure 5.4. CM between ethyl vinyl ether and initiator **A***

When a 10-fold excess of 2-*iso*-propoxystyrene is added to initiator **A**, 50 % of the ruthenium complex is immediately converted to $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)$ (*Figure 3.2*, **F**), the kinetic product. After 48 hours of reaction, this complex, and a trace of $RuCl_2(PCy_3)_2(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)$ (*Figure 3.2*, **G**), are the only alkylidene complexes observed by ^1H NMR spectroscopy. The absence of the thermodynamic methylidene product may again be attributed to oxygen chelation to the ruthenium centre.

Conversely, when 10 equivalents of styrene are added to initiator **A**, there is no immediate change in appearance of the alkylidene region of ^1H NMR spectra. However, over a 48 hour period the thermodynamic product, $RuCl_2(PCy_3)_2(=CH_2)$, gradually appears and eventually becomes the exclusive species present. In this case, formation of the thermodynamic product is not impeded by oxygen chelation to the ruthenium centre.

CM between disubstituted alkenes (*trans*-3-hexene, *cis*-stilbene and *cis*-2,2'-dimethoxystilbene, *Figure 5.5*) and initiator **A** has also been investigated. After 10 minutes of reaction with *trans*-3-hexene, 92 % of initiator **A** is converted to $RuCl_2(PCy_3)_2(=CHEt)$ and over the following 48 hours $RuCl_2(PCy_3)_2(=CH_2)$ is not observed. It is not clear if initiator **A** undergoes CM with *cis*-stilbene due to the product of the reaction being initiator **A** and hence there is no change in appearance of the alkylidene region of ^1H NMR spectra. However, it is clear that *cis*-2,2'-dimethoxystilbene does not. This may be attributed to a large steric bulk on either side of the double bond impeding the formation of the metallacyclobutane species.

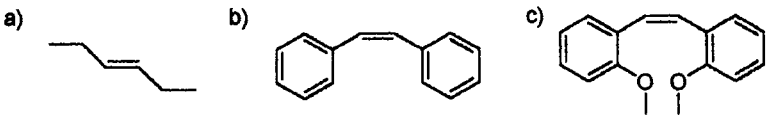

Figure 5.5 disubstituted acyclic olefins a) trans-3-hexene, b) cis-stilbene and c) cis-2,2'-dimethoxystilbene

In summary, terminal acyclic olefins readily undergo CM with initiator **A** to form substituted ruthenium alkylidene complexes, the kinetic product. If the olefin contains ethereal oxygen in close proximity to the double bond then this is the only species observed. If it does not, then the thermodynamic methylidene complex may appear in the system over time. The rate at which a disubstituted olefin undergoes CM with initiator **A** is dependant on the steric hindrance present either side of the double bond, and the formation of $RuCl_2(PCy_3)_2(=CH_2)$ is prohibited due to the absence of terminal alkenes in the system.

5.3 The Induced Regeneration of Metathesis Catalyst from ROMP Systems using Terminal Olefins

As described in section 2.2, when polymerisations mediated by initiator **A** are terminated with ethyl vinyl ether, the exclusive formation of $RuCl_2(PCy_3)_2(=CHOEt)$ and a $[CH_2]$ end-capped polymer is observed.[13] Theoretically, ethyl vinyl ether can insert into the ruthenium-carbon double bond in two different orientations, but the formation of intermediate α_{pol} is preferred over intermediate β_{pol} due to the two substituents (OEt and R_{pol}) being in the 1,3 position, hence reducing their steric interaction (*Figure 5.6*).

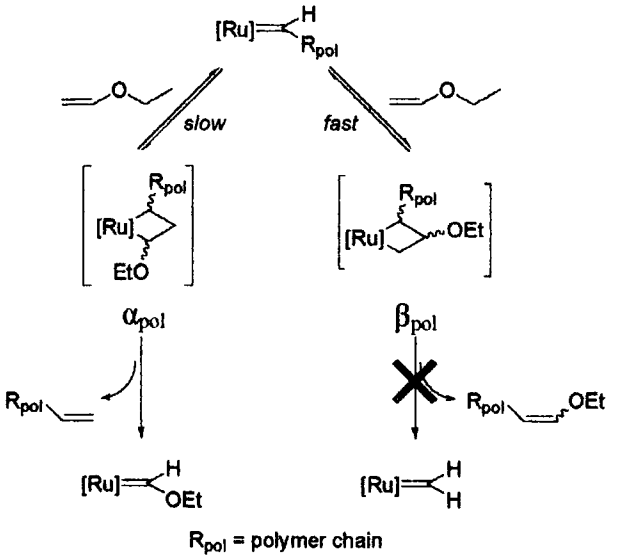

Figure 5.6. The possible orientations in which ethyl vinyl ether can undergo CM with propagating ruthenium alkylidene species

Therefore, theoretically if ROMP reactions mediated by initiator **A** are terminated with terminal acyclic olefins of the general formula CH_2=CHX, then the resultant polymer will be end-capped with [CH_2] giving rise to ruthenium alkylidene species of the type $RuCl_2(PCy_3)_2$(=CHX). If this holds true, then careful consideration of the terminating agent used, instead of the habitual use of ethyl vinyl ether, could result in the formation of active metathesis ruthenium alkylidene complexes. The recovery and re-use of these initiators in subsequent olefin metathesis reactions would, in financial terms, make ROMP reactions more appealing.

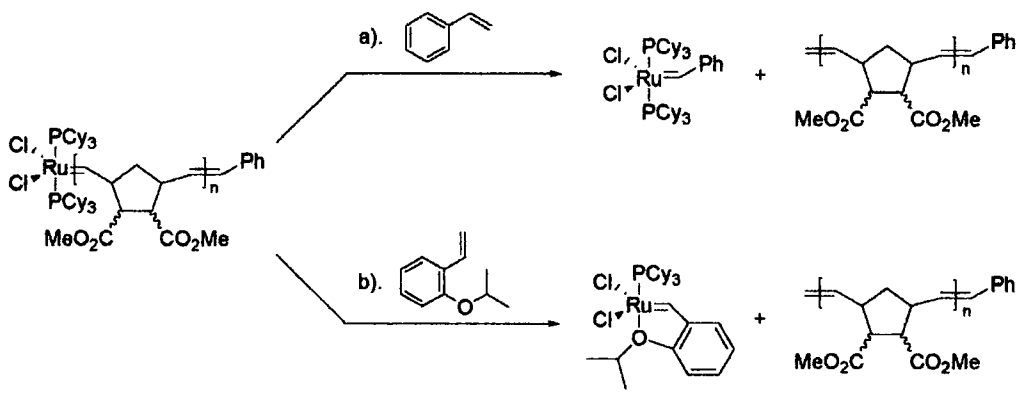

*Figure 5.7. The formation of initiator **A** or initiator **F** by CM between propagating ruthenium alkylidene species and a) styrene or b) 2-iso-propoxystyrene, respectively*

Of immediate interest is the use of terminating agents such as a) styrene leading to regeneration of initiator **A** or b) 2-*iso*-propoxystyrene, which would give rise to initiator **F**, Hoveyda's catalyst (*Figure 5.7*).

5.3.1 Regeneration and Recovery of Initiator A

When the ROMP of *exo,endo*-5,6-dicarbomethoxynorbornene (*Figure 2.2*, **2a**) is mediated by initiator **A**, using $[M]_o/[I]_o = 20$ in $CDCl_3$, more than 95 % of initiator **A** is consumed, and the monomer is polymerised over a period of 5 hours. During the polymerisation, two sets of two propagating species (**IIa** and **IIIa**) appear in the alkylidene region of the ^1H NMR spectrum alongside residual initiator **A** (*Figure 5.8a*). The resonances assigned as **IIa** correspond to the protons of the propagating alkylidene species, with the proximal backbone double bond either *cis* or *trans*, in which a pair of PCy_3 ligands are bound to the ruthenium centre, whereas the resonances of **IIIa** correspond the equivalent species with only one PCy_3 ligand, the remaining co-ordination site being occupied by an oxygen atom emanating from the polymer backbone (Chapter 4).

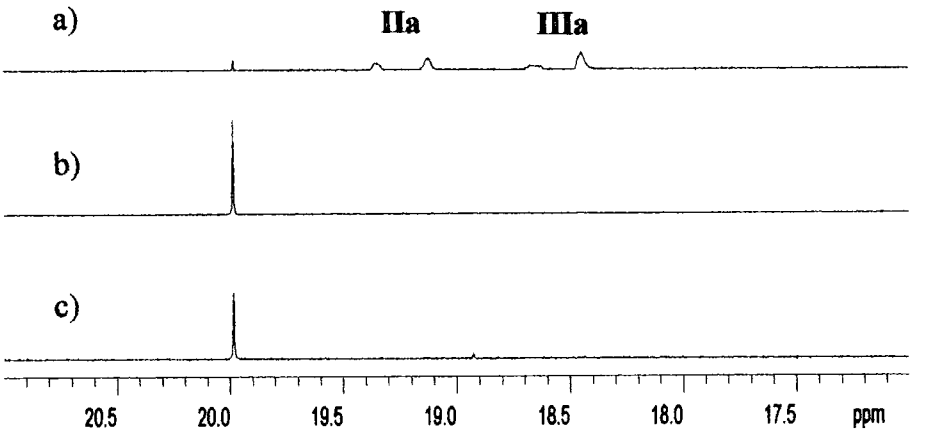

*Figure 5.8. The alkylidene region of 500 MHz ^1H NMR spectra ($CDCl_3$) after a) 5 hours of reaction when **2a** is subjected to ROMP by initiator **A**, and b) 2 hours, and c) 6 hours after the addition of styrene (2 equiv.). $[M]_o/[I]_o=20$, $[I]_o=15$ mM*

The addition of styrene (2 equivalents) to the reaction mixture results in a dramatic change in the appearance of the alkylidene region of the ^1H NMR spectrum. After 2 hours of reaction, CM between styrene and the propagating alkylidene species results exclusively in the regeneration of initiator **A**, the kinetic product (*Figure 5.8b*). Initiator **A** was recovered from the reaction mixture in an unquantitative manner in

relatively good yields (37 %). The rate at which CM occurs can be enhanced by the addition of a larger excess of styrene. In the case of 5 added equivalents, the propagating species are completely and exclusively converted to initiator **A** after only 10 minutes. If the regenerated initiator is not immediately recovered, then thermodynamic formation of $RuCl_2(PCy_3)_2(=CH_2)$ is observed through the appearance of a characteristic resonance at 18.92 ppm (*Figure 5.8c*).

The recovered initiator can be successfully re-used in subsequent metathesis reactions. For example, when used to mediate the ROMP of monomer **2a** using $[M]_o/[I]_o = 20$, it behaves in a comparable manner to a fresh batch of initiator **A**. Monomer **2a** is consumed over a period of 5 hours, and the resulting polymer has a PDI = 1.12 and M_n = 3,472 (predicted 4,200). It is also capable of ring-closing 20 equivalents of diethyl diallylmalonate in less than 30 minutes.

5.3.2 Formation and Recovery of Initiator F

In the same manner as described above, initiator **F** can be formed and recovered from the ROMP of monomer **2a** mediated by initiator **A**, using $[M]_o/[I]_o = 20$ in $CDCl_3$. The only difference in this system is the use of 2-*iso*-propoxystyrene as the terminating agent instead of styrene. The reaction can be followed by ^1H NMR spectroscopy.

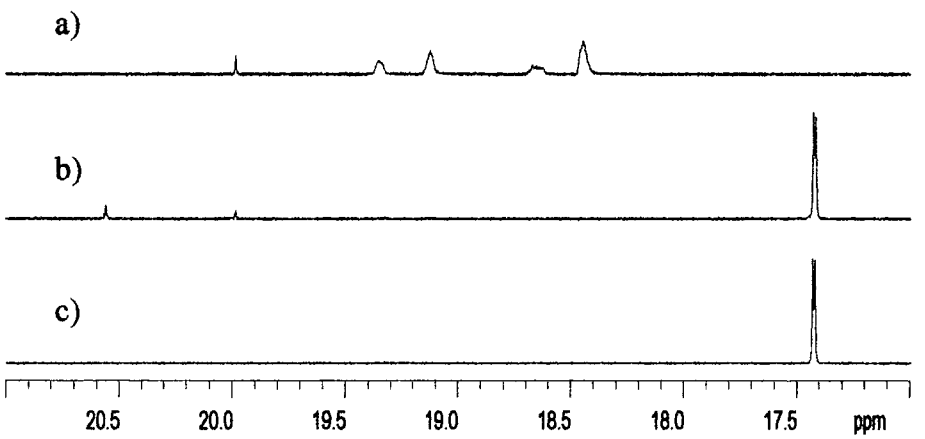

*Figure 5.9. The alkylidene region of 500 MHz ^1H NMR spectra ($CDCl_3$) after a) 5 hours of reaction when **2a** is subjected to ROMP by initiator **A**, and b) 45 minutes, and c) 24 hours after the addition of 2-iso-propoxystyrene (2 equiv.). $[M]_o/[I]_o=20$, $[I]_o=15$ mM*

Figure 5.9a shows the appearance of the propagating alkylidene species in the alkylidene region of the ^{1}H NMR spectrum obtained upon complete consumption of monomer **2a** by initiator **A**. The alkylidene region of the reaction mixture 45 minutes after the addition of 2-*iso*-propoxystyrene (2 equivalents) is shown in *Figure 5.9b*. The characteristic doublet of initiator **F** can be seen at 17.44 ppm as the major alkylidene species (92 %) and residual initiator **A** is observed at 19.99 ppm (2 %). The resonance at 20.55 ppm corresponds to that of initiator **G** which forms due to the presence of a stoichiometric amount of free PCy_3 in the system (*Figure 5.10*).

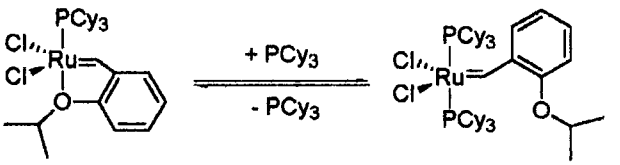

*Figure 5.10. The equilibrium that exists between initiator **F** and initiator **G** in the presence of PCy_3*

If the reaction mixture is left over an extended period of time, the resonances corresponding to initiator **G** and initiator **A** disappear, and initiator **F** remains as the only alkylidene species present (*Figure 5.9c*). The formation of $RuCl_2(PCy_3)_2(=CH_2)$ is not observed.

Initiator **F** can be recovered from the reaction mixture in good yields (77 %) and re-used in subsequent olefin metathesis reactions. For example, it is capable of ring-closing 20 equivalents of diethyl diallylmalonate in 3 hours, and when used to mediate the ROMP of monomer **2a** using $[M]_o/[I]_o = 20$, the monomer is consumed in 9 hours and the resulting polymer has a PDI = 1.32 and M_n = 4,040 (predicted 4200). The slower rate of monomer consumption relative to a 'fresh' batch of initiator **F** may be attributed to the presence of excess PCy_3, which is known to inhibit the rates of initiation and propagation (Section 3.5.3).[14] The excess of phosphine, originating from initiator **A**, remains due to its solubility in hexane, and it is therefore not completely removed in the process of recovering the catalyst.

This method is very attractive since it allows the formation and recovery of initiator **F** from a ROMP reaction mediated by initiator **A**, and the recovery process can be performed on the bench using standard grade solvents and silica gel chromatography.

5.3.3 General Method for Induced Regeneration and Recovery of Olefin Metathesis Complexes

The use of the technique described above coupled with the appropriate choice of terminating agent, could potentially result in the recovery of any derivative of complexes of the type $RuCl_2(PCy_3)_2(=CHR)$ (where R is the functionality introduced by the terminating agent) from the polymerisation of any monomer mediated by initiator **A**. As shown in *Figure 5.11*, this results in a catalytic cycle from which ruthenium complexes can be recovered and used in subsequent olefin metathesis reactions. This is a vast improvement on the single batch processes currently associated with olefin metathesis reactions mediated by complexes similar to initiator **A**, where the active catalytic species is 'lost' once the reaction reaches completion.

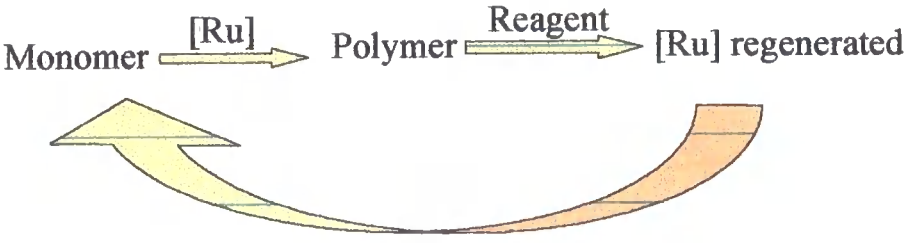

Figure 5.11. Catalytic cycle for well-defined ruthenium initiators

5.4 Induced Formation of Metathesis Catalysts from ROMP Systems Using Disubstituted Olefins

When styrene is used to induce regeneration of the initiator from the ROMP of monomer **2a** mediated by initiator **A**, the formation of the thermodynamic methylidene product is observed if the reaction mixture is left over an extended time period. In an attempt to eliminate the formation of $RuCl_2(PCy_3)_2(=CH_2)$, disubstituted acyclic olefins (*Figure 5.5*) were added to the ROMP system once the monomer had been consumed instead of terminal olefins.

5.4.1 The use of *cis*-stilbene as a Terminating Agent

The addition of *cis*-stilbene to the ROMP of monomer **2a** mediated by initiator **A** results in the regeneration of the original ruthenium complex. *Figure 5.12* shows the alkylidene region of the ^1H NMR spectra at various times after the addition of 20 equivalents of *cis*-stilbene to the system. Unfortunately the CM reaction between *cis*-stilbene and the propagating ruthenium species take place extremely slowly. Only 20

% of initiator **A** has been regenerated after 48 hours of reaction. The slow formation of initiator **A** is attributed to the high degree of steric hindrance that arises during formation of the metallacylobutane species. Obviously this is not a convenient rate at which to regenerate the initiator.

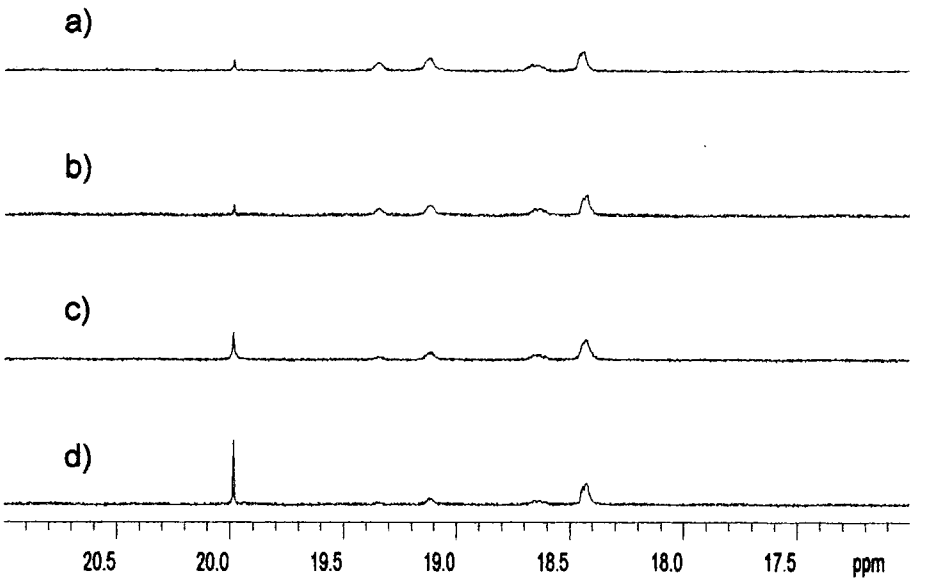

*Figure 5.12. The alkylidene region of 500 MHz ^1H NMR spectra ($CDCl_3$) after a) 5 hours of reaction when **2a** is subjected to ROMP by initiator **A**, and b) 30 mins, c) 24 hrs, and d) 48 hrs after the addition of cis-stilbene (20 equiv.) .$[M]_o/[I]_o$=20, $[I]_o$=15mM*

5.4.2 The use of *cis*-2,2'-dimethoxystilbene as a Terminating Agent

In an attempt to induce the formation of $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O\text{-}MeC_6H_4)$ (a derivative of initiator **F**) from the ROMP of monomer **2a** mediated by initiator **A**, the disubstituted acyclic olefin, *cis*-2,2'-dimethoxystilbene was added to the system once the monomer had been consumed. CM between the acyclic olefin and the propagating species did not occur, even when a 20-fold excess of *cis*-2,2'-dimethoxystilbene was used. This is attributed to the formation of the metallacyclobutane species being prohibited by a large steric interaction between the two reactants.

5.5 Induced Regeneration of Metathesis Catalysts from RCM Systems

This chapter has introduced the development of a technique which allows active metathesis complexes to be formed and recovered from ROMP reactions mediated by

initiator **A**. The recovered complexes are active for use in subsequent olefin metathesis reactions.

RCM of diene derivatives mediated by ruthenium alkylidene complexes has been the subject of recent interest.[6-11] Initiator **A** and initiator **F** are known to be efficient, in terms of turnover, for performing RCM. Therefore, if it is possible to extend the method of inducing regeneration of initiators described earlier into RCM systems, then the scope of this new technique will be significantly increased.

5.5.1 The Mechanism of RCM

The RCM of organic molecules containing two double bonds is similar to ROMP in the fact that both reactions are mediated by alkylidene complexes. When a ruthenium alkylidene complex is used, it undergoes a [2+2] cyclo-addition with a double bond of the diene to form a metallacyclobutane.[3] Productive cleavage of this four-membered species gives rise to a new alkylidene species and the elimination of a small organic by-product (*Figure 5.13*). The double bond which remains from the original diene then undergoes olefin metathesis with the new ruthenium alkylidene species, which gives rise to the formation of a ring-closed organic molecule and a ruthenium methylidene species. The methylidene species then mediates the RCM of the unreacted diene remaining in the system.

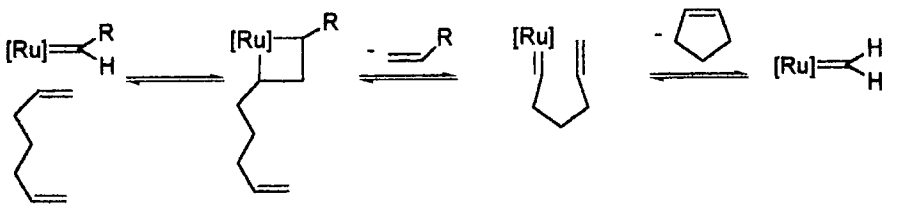

Figure 5.13. The general mechanism of RCM

5.5.2 RCM Mediated by Initiator A

When initiator **A** is used to perform RCM reactions, for each cycle that a monomer unit is ring-closed, a stoichiometric amount of ethene is expelled. When all of the substrate has been successfully ring-closed, the active $RuCl_2(PCy_3)(=CH_2)$ species recombines with PCy_3 to form $RuCl_2(PCy_3)_2(=CH_2)$, which remains as the only ruthenium alkylidene species in solution (*Figure 5.14*). The ruthenium methylidene can perform RCM if another batch of diene is added.

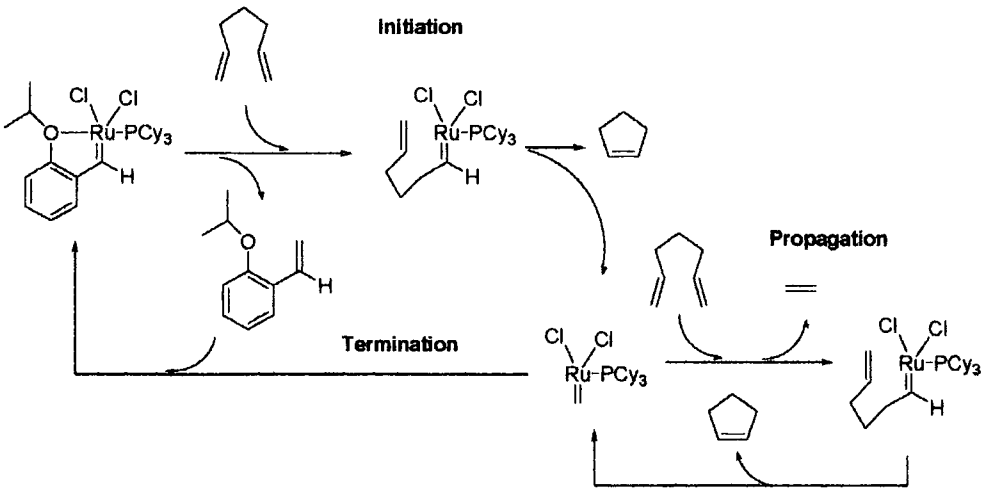

Figure 5.14. The mechanism of RCM mediated by initiator A

5.5.3 RCM Mediated by initiator F

When initiator **F** is used to mediate RCM reactions, the chelating oxygen atom from the benzylidene moiety dissociates from the ruthenium centre in order for the diene to undergo a [2+2] cyclo-addition reaction.[15] Productive cleavage of the metallacyclobutane results in the formation of a new ruthenium alkylidene species and the elimination of a stoichiometric amount of 2-*iso*-propoxystyrene (*Figure 5.15*).

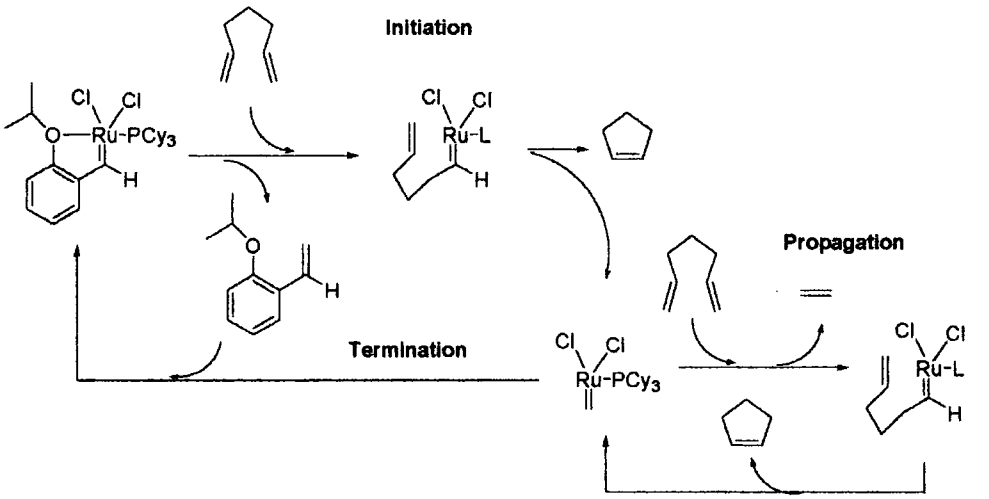

Figure 5.15. The mechanism of RCM mediated by initiator F

From this point onwards, the reaction proceeds in exactly the same manner as that described for initiator **A**. The only difference being that at the end of the RCM reaction, the mono(phosphine) ruthenium methylidene species undergoes CM with 2-*iso*-propoxystyrene to regenerate initiator **F**.

5.5.4 RCM of Diethyl diallylmalonate using Initiator A

Diethyl diallylmalonate is a bench-mark substrate commonly subjected to RCM by well-defined ruthenium initiators.[16,17] When initiator **A** is used to mediate the RCM reaction of 20 equivalents of diethyl diallylmalonate, the diene is ring-closed after only 30 minutes of reaction. Upon completion of the reaction, $RuCl_2(PCy_3)_2(=CH_2)$ (98 %) and initiator **A** (2 %) remain in solution (*Figure 5.16, step a*). If another 20 equivalents of diethyl diallylmalonate are added to the reaction, it is ring-closed but at a considerably slower rate (*Figure 5.16, step b*). This is attributed to $RuCl_2(PCy_3)_2(=CH_2)$ being less active for RCM than $RuCl_2(PCy_3)(=CH_2)$.

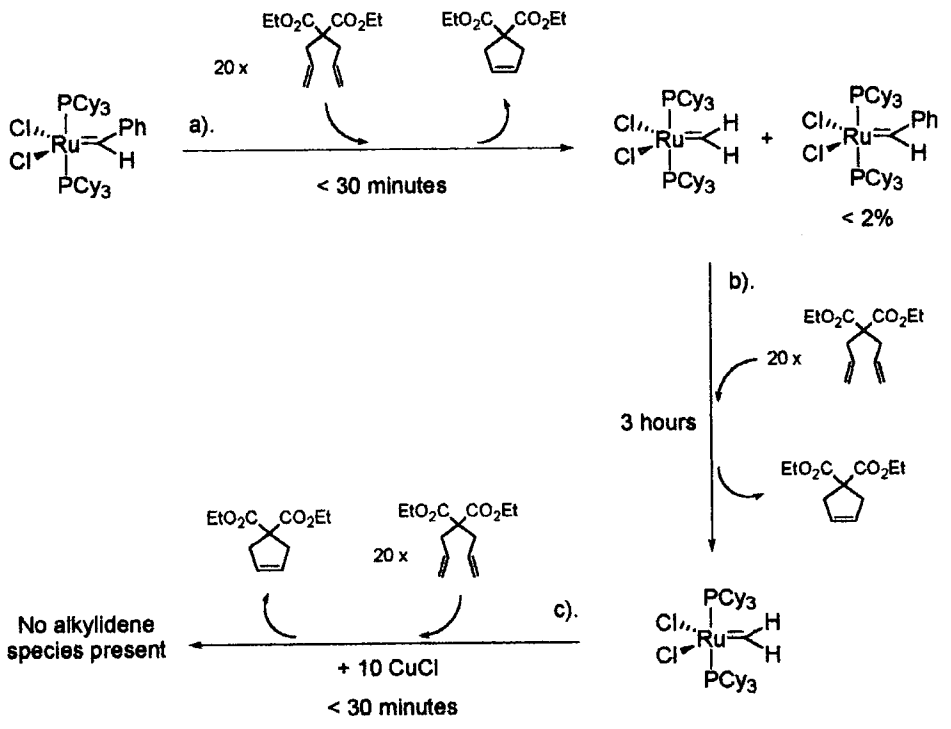

Figure 5.16. Multiple RCM reactions mediated by initiator A

The addition of another batch of diethyl diallylmalonate along with 10 equivalents of CuCl (a phosphine 'sponge') results in the diene being ring-closed in less than 30 minutes (*Figure 5.16, path c*). CuCl is capable of trapping labile PCy_3 ligands, and hence generates a more active RCM species, $RuCl_2(PCy_3)(=CH_2)$.[18] After RCM is complete, no species are observed in the alkylidene region of the ^1H NMR spectra. This is attributed to mono(phosphine) alkylidene species being unstable and therefore going through a decomposition pathway described earlier.[18]

5.5.5 Induced Regeneration of Metathesis Catalysts in RCM systems

In order to induce the formation of active metathesis complexes from RCM systems mediated by initiator **A**, the regenerating agent, an acyclic olefin, must undergo CM with $RuCl_2(PCy_3)_2(=CH_2)$, the alkylidene species present in solution once the RCM reaction reaches completion (*Figure 5.17*). The addition of 5 equivalents of styrene, *trans*-3-hexene or *cis*-stilbene to the reaction mixture does not result in a CM with the ruthenium methylidene complex. The use of 2-*iso*-propoxystyrene as the terminating agent gives rise to initiator **F**. However, the rate at which this occurs is extremely slow, and after 24 hours of reaction, only 25 % of $RuCl_2(PCy_3)_2(=CH_2)$ is converted to initiator **F**.

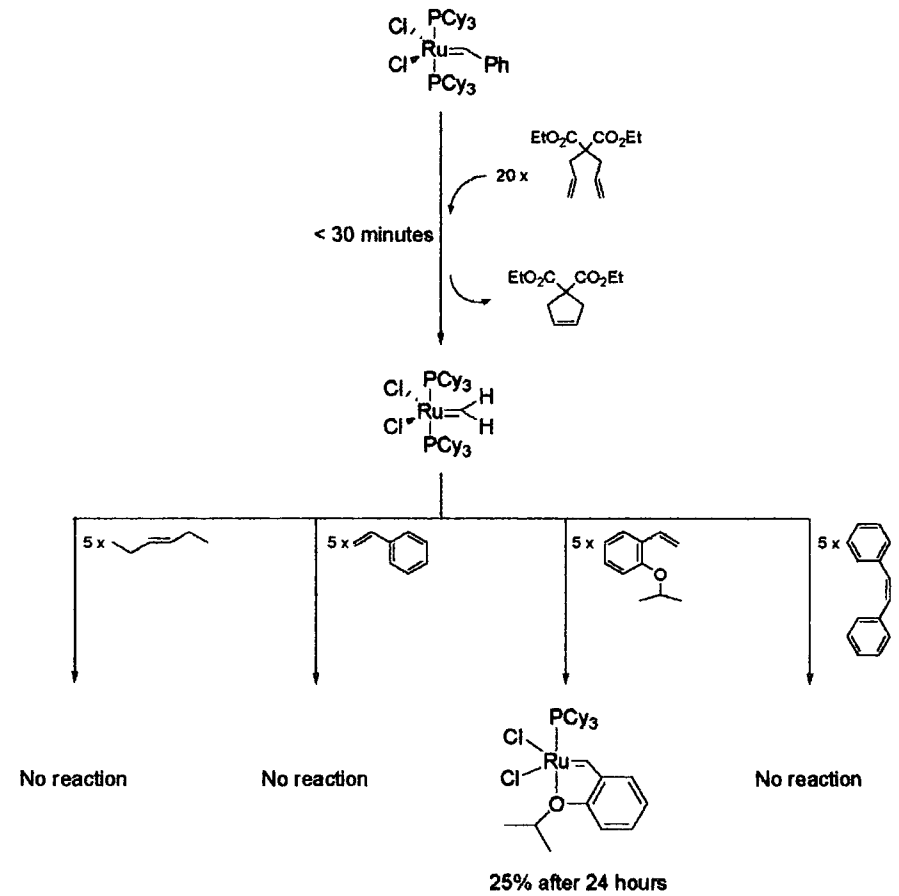

*Figure 5.17. CM between acyclic terminating agents and $RuCl_2(PCy_3)_2(=CH_2)$, after the RCM of diethyl diallylmalonate is mediated by initiator **A***

It is reported that when initiator **F** is used to mediate the RCM of organic molecules, the 2-*iso*-propoxystyrene moiety is cleaved from the ruthenium metal centre and then recombines with the active mono(phosphine) ruthenium methylidene species to regenerate initiator **F** (Section 5.5.3).[15] In an attempt to apply this *in situ* regeneration

of the initiator to RCM reactions mediated by initiator **A**, the regenerating agent was added to initiator **A** before the RCM of diethyl diallylmalonate was started. The theory being that with the terminating agent present in the system at the point of completion of the RCM reaction, it should react with $RuCl_2(PCy_3)(=CH_2)$ and induce the formation of the desired ruthenium alkylidene species.

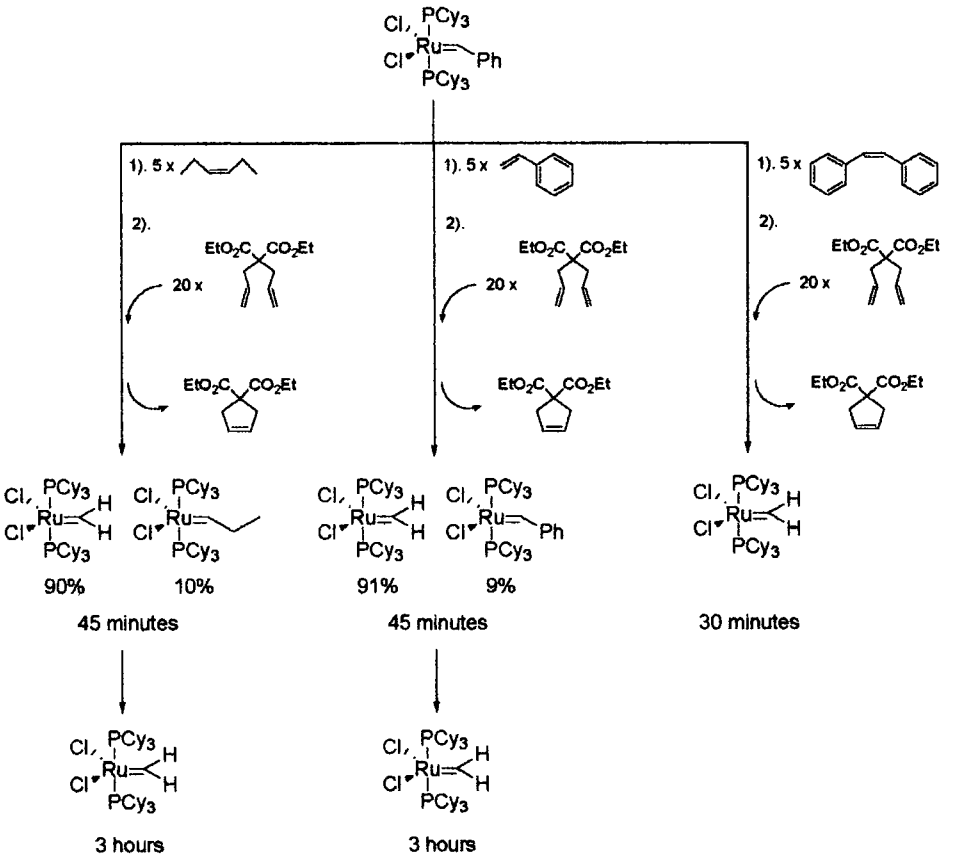

Figure 5.18. The attempted in situ formation of ruthenium alkylidene complexes during RCM of diethyl diallylmalonate mediated by initiator A

The addition of non-oxygen-containing terminating agents to initiator **A** before it was used to mediate RCM of diethyl diallylmalonate, was found to have no measurable effect on the rate at which RCM proceeded. The use of *trans*-3-hexene or styrene resulted in conversion of ~10 % of the methylidene species to $RuCl_2(PCy_3)_2(=CHEt)$ and initiator **A**, respectively, at the end of the reaction. However, after 3 hours of reaction, only the thermodynamic product, $RuCl_2(PCy_3)_2(=CH_2)$, was present (*Figure 5.18*). When *cis*-stilbene was used as the terminating agent, only $RuCl_2(PCy_3)_2(=CH_2)$ was seen in the alkylidene region of ^1H NMR spectra during and after ring-closing of the substrate, indicating that the methylidene species was unreactive towards *cis*-stilbene (*Figure 5.18*).

The presence of 2-*iso*-propoxystyrene during the RCM of diethyl diallylmalonate mediated by initiator **A** retarded the rate at which the substrate was ring-closed. After 45 minutes of reaction, 75 % of unreacted diethyl diallylmalonate remained in solution, and a mixture of four ruthenium complexes [**A**, **F**, **G** and $RuCl_2(PCy_3)_2(=CH_2)$] were observed in the alkylidene region of the ^1H NMR spectrum (*Figure 5.19*). It took 30 hours for all of the diethyl diallylmalonate to be ring-closed, after which time only complexes $RuCl_2(PCy_3)_2(=CH_2)$ and initiator **F** were present.

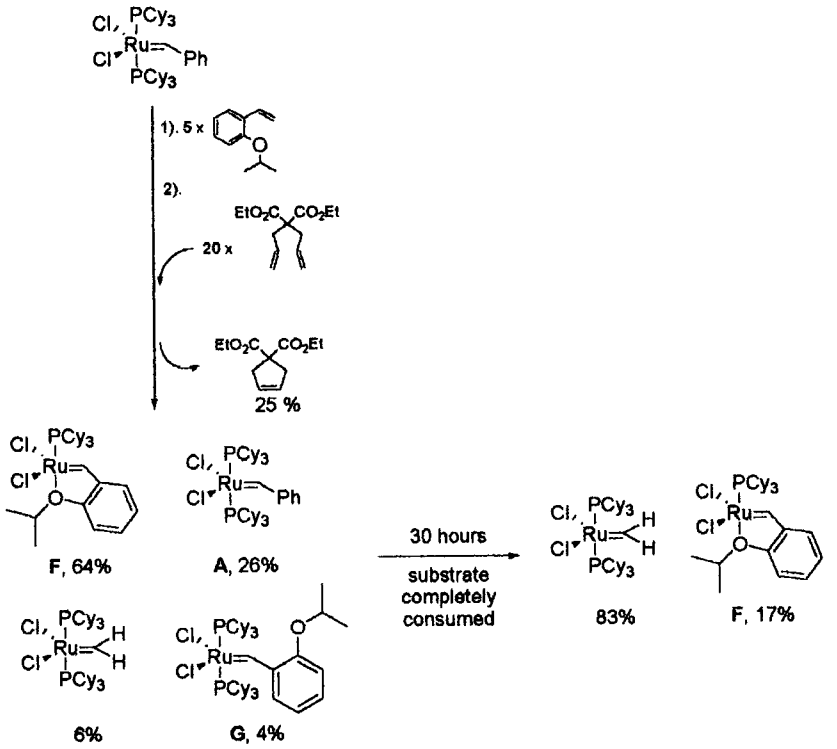

*Figure 5.19. The attempted in situ formation of initiator **F** during RCM of diethyl diallylmalonate mediated by initiator **A***

The observation that $RuCl_2(PCy_3)_2(=CH_2)$ as the sole alkylidene species remaining in solution after initiator **A** has mediated the RCM of dienes, means that the formation of ruthenium alkylidene complexes can not be induced by the addition of acyclic olefins under these reaction conditions.

5.6 Summary

A novel methodology that permits the induced formation and recovery of well-defined complexes from ROMP reactions mediated by initiator **A** has been developed. The ruthenium alkylidene complexes are formed by the addition of acyclic olefinic

terminating agents once the polymerisation reaches completion. The complexes can be recovered in good yields and are found to be active for use in subsequent olefin metathesis reactions.

The appropriate choice of terminating agent permits the induced regeneration of any derivative of $RuCl_2(PCy_3)_2(=CHR)$, where R is the functionality introduced by the terminating agent.

This method of inducing the formation of metathesis complexes from olefin metathesis reactions mediated by initiator **A** is attractive in financial terms. The simple addition of a terminating agent to a ROMP reaction converts the expensive non-recyclable ruthenium initiator into a cost effective re-usable catalyst.

Attempts to induce regeneration of well-defined complexes from RCM reactions mediated by initiator **A** proved to be unsuccessful. This is due to low levels of CM occuring between the ruthenium alkylidene species present in solution at the end of the catalytic cycle, $RuCl_2(PCy_3)_2(=CH_2)$, and acyclic olefinic terminating agents.

5.7 References

1. D. M. Haigh, A. M. Kenwright, E. Khosravi, *Tetrahedron* **2004**, *60*, 7217.
2. P. Schwab, R. H. Grubbs, J. W. Ziller, *Journal of the American Chemical Society* **1996**, *118*, 100.
3. M. S. Sanford, J. A. Love, R. H. Grubbs, *Journal of the American Chemical Society* **2001**, *123*, 6543.
4. O. A. Scherman, H. M. Kim, R. H. Grubbs, *Macromolecules* **2002**, *35*, 5366.
5. E. Khosravi, W. J. Feast, A. A. Al-Hajaji, T. Leejarkpai, *Journal of Molecular Catalysis A: Chemical* **2000**, *160*, 1.
6. S. J. Miller, H. E. Blackwell, R. H. Grubbs, *Journal of the American Chemical Society* **1996**, *118*, 9606.
7. T. A. Kirkland, R. H. Grubbs, *Journal of Organic Chemistry* **1997**, *62*, 7310.
8. A. Fuerstner, O. R. Thiel, *Journal of Organic Chemistry* **2000**, *65*, 1738.
9. M. Arisawa, H. Kaneko, A. Nishida, M. Nakagawa, *Journal of the Chemical Society, Perkin Transactions 1* **2002**, 959.
10. A. Nayek, S. Banerjee, S. Sinha, S. Ghosh, *Tetrahedron Letters* **2004**, *45*, 6457.

11. J. R. Del Valle, M. Goodman, *Journal of Organic Chemistry* **2004**, *69*, 8946.
12. M. R. Buchmeiser, *New Journal of Chemistry* **2004**, *28*, 549.
13. K. J. Ivin, A. M. Kenwright, E. Khosravi, J. G. Hamilton, *Macromolecular Chemistry and Physics* **2001**, *202*, 3624.
14. C. W. Bielawski, R. H. Grubbs, *Macromolecules* **2001**, *34*, 8838.
15. J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus, Jr., A. H. Hoveyda, *Journal of the American Chemical Society* **1999**, *121*, 791.
16. E. L. Dias, S. T. Nguyen, R. H. Grubbs, *Journal of the American Chemical Society* **1997**, *119*, 3887.
17. M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Letters* **1999**, *40*, 2247.
18. M. Ulman, R. H. Grubbs, *Journal of Organic Chemistry* **1999**, *64*, 7202.

Chapter 6

General Conclusions and Further Work

6.1 General Conclusions

The remarkable observation of regeneration of the initiator apparent when 7-*tert*-butoxynorbornadiene (*Figure 2.2*, **1**) was subjected to ROMP mediated by $RuCl_2(PCy_3)_2(=CHPh)$ (*Figure 2.1*, **A**) has been investigated, and the parameters which govern this process have been studied.

It has been established that regeneration of the initiator is exclusive to systems in which the monomers contained oxygen in the 7-position and the polymerisation was mediated by initiator **A**. It was found that subtle changes to the chemical nature of the ligands of the ruthenium complex results in no regeneration of the initiator being observed. Similarly, if the monomer did not contain oxygen functionality in the 7-position then the process was prohibited.

The extent of regeneration of the initiator apparent when 7-alkoxynorbornadiene monomers (**1** and **5-7**) were subjected to ROMP mediated by initiator **A** was found to decrease as the steric bulk of the substituent in the 7-position was decreased. A decrease in the ratio of $[M]_o/[I]_o$ was also found to reduce the extent of regeneration that was observed. A change in the polarity of the solvent had no significant effect on the extent of regeneration of the initiator, but as the polarity of the solvent was reduced, the overall kinetics for the polymerisation process were retarded.

The observation of regeneration of the initiator during the ROMP of 7-alkoxynorbornadiene monomers mediated by initiator **A** occurs via either intra- or inter-molecular secondary metathesis reactions at the propagating polymer chain-ends. However, it was identified that there are nine possible ways in which the ruthenium alkylidene can react with double bonds (internal or terminal) in the propagating polymer backbone, and only two of these secondary metathesis reactions result in regeneration of the initiator. This was confirmed by monitoring the alkylidene region of ^1H NMR spectra when 7-neopentylnorbornadiene (*Figure 3.2*, **12a**) and monomer **1** were subjected to a block copolymerisation mediated by initiator **A**.

It was not possible to conclusively determine whether intra- and/or inter-molecular reactions were responsible for the observed regeneration of the initiator using MALDI-TOF MS. This was due to insufficient ionisation of the polymer preventing its successful projection through the spectrometer. Attempts to prepare modified monomers, of which resulting polymers would be more suited to characterisation by MALDI-TOF MS, were also unsuccessful.

During the ROMP of monomer **1** mediated by initiator **A**, two propagating alkylidene species were observed by ^{1}H NMR spectroscopy. A triplet (**Ib**, 19.38, 19.36, 19.33 ppm) appeared alongside a small amount of another species (**IIb**) which gave rise to a broad signal at ~17.5 ppm. The identity of these species was determined by the addition of free phosphines and phosphine scavengers to the reaction upon complete consumption of the monomer. Species of the type **Ib**, which diminished at the expense of the regenerated initiator, were found to be bis(phosphine) propagating species, whereas **IIb** were found to be mono(phosphine) species in which the vacant co-ordination site at the ruthenium centre was occupied by an oxygen atom emanating from the propagating polymer backbone. Molecular modelling revealed that oxygen chelation to the ruthenium centre from the immediately adjacent monomer unit only occurred if the double bond *syn* to the 7-alkoxy substituent was opened.

The ROMP reactions of a variety of bicyclic monomers initiated by initiator **A** were performed, and the nature of propagating alkylidene species that arose have been unambiguously identified. In all of the systems studied, bis(phosphine) species were observed. In systems where the monomer contains oxygen, additional propagating signals were apparent. The exact chemical shift and multiplicity of these resonances was found to be dependent on the specific position and nature of the oxygen-containing functional groups. These additional signals have been attributed to mono(phosphine) species in which oxygen from the propagating polymer backbone chelates to the ruthenium centre.

Species of the type **IIb** were found to be extremely stable in solution, and active for olefin metathesis. $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)$ (*Figure 3.2*, **F**) is an extremely stable ruthenium complex containing internal oxygen chelation. Selective ^{31}P NMR decoupling experiments revealed that the broad resonance at ~17.5 ppm (**IIb**) was a mono(phosphine) oxygen-chelated species similar in structure to initiator **F**, providing further evidence for oxygen chelation to the ruthenium centre.

The ligand exchange and ROMP behaviour of initiator **F** was studied. In the presence of free PCy_3, the chelating oxygen atom of initiator **F** was displaced to give rise to an *iso*-propoxy-substituted benzylidene analogue of initiator **A**. Polymerisations mediated by initiator **F** proceeded more slowly than those mediated by initiator **A**, and the extent of initiation was found to be lower. Bis(phosphine) propagating species were not present due to the absence of a stoichiometric amount of PCy_3. When monomers containing oxygen were subjected to ROMP mediated by initiator **F**,

mono(phosphine) propagating species were observed. During the ROMP of hydrocarbon monomers mediated by initiator **F** propagating resonances were not apparent due to the absence of both oxygen in the polymer backbone and free PCy_3 to chelate to the ruthenium centre.

The relationship between the process of regeneration of the initiator and chelation of oxygen from the propagating polymer backbone to the ruthenium centre was probed by ^1H and ^{31}P NMR spectroscopy. It was established that oxygen chelation to the ruthenium centre was prevented by the addition of PCy_3, and an increase in concentration of PCy_3 coincided with a reduction in the extent of regeneration of the initiator observed. Although no direct relationship between the formation of mono(phosphine) oxygen chelated species and regeneration of the initiator was established, it is worthy of note that the only systems in which the phenomenon of regeneration was observed coincided with oxygen chelation to the ruthenium centre from the immediately adjacent monomer unit. This highlights that it is specifically the presence of 7-alkoxy groups contained within the monomer which facilitate the regeneration process.

Consideration of the mechanism by which regeneration of the initiator occurred and the manner in which ethyl vinyl ether reacts with propagating alkylidene species, coupled with the appropriate choice of terminating agent, resulted in the development of a technique which permits the regeneration of ruthenium alkylidene complexes to be induced from potentially any ROMP system mediated by initiator **A**. Ruthenium alkylidene complexes were recovered in good yields and were found to be active for mediating subsequent olefin metathesis reactions. This method of inducing the formation of active metathesis complexes from olefin metathesis reactions mediated by initiator **A** is financially attractive. The simple addition of a terminating agent to a ROMP reaction results in the expensive non-recyclable ruthenium initiator being converted into a cost effective re-usable catalyst.

6.2 Future Work

The following sections outline areas of research, based on the findings reported in this thesis, which might be of interest to further study.

6.2.1 The ROMP of 7-alkoxynorbornene Monomers

Regeneration of the initiator was observed when 7-alkoxynorbornadiene monomers were subjected to ROMP mediated by initiator **A**. It was proposed that the mono(phosphine) oxygen-chelated propagating species observed at ~17.5 ppm during these reactions could only form when the monomer unit immediately adjacent to the ruthenium centre had been ring-opened via the double bond *syn* to its alkoxy substituent (Section 3.6.1). ^{13}C NMR spectroscopic studies revealed that these polymerisations proceeded predominantly by opening of the double bond which was *anti* to the alkoxy substituent, and therefore it is possible that the minor amounts of mono(phosphine) propagating species observed formed as a result of *syn* enchainment.[1]

To explore this phenomenon further, *syn*- and *anti*-7-alkoxynorbornene monomers could be prepared and subjected to ROMP by initiator **A**. If the above theory is correct, then it would be expected that polymerisation of the *anti* monomer would be fast, and no mono(phosphine) oxygen-chelated propagating species would be observed, due to *syn* enchainment being prohibited. The polymerisation of the *syn* monomer may be slow due to the formation of the mono(phosphine) oxygen chelated species.

It will be interesting to note whether these systems exhibit regeneration of the initiator, and it is hoped that the results will give further insight to whether oxygen chelation to the ruthenium centre during ROMP does facilitate the regeneration process.

6.2.2 The ROMP of 5-alkoxynorbornene Monomers

In order to investigate whether the specific position of the alkoxy functionality contained within bicyclic olefin monomers effected the process of regeneration of the initiator and the ability of oxygen from the propagating polymer backbone to chelate to the ruthenium centre, the ROMP of *exo*-5-methoxymethylnorbornene (**8**) and *exo,exo*-5,6-bis(methoxymethyl)norbornene (**9**) were mediated by initiator **A** (*Figure*

6.1). Neither regeneration of the initiator or oxygen chelated propagating species were observed in these systems.

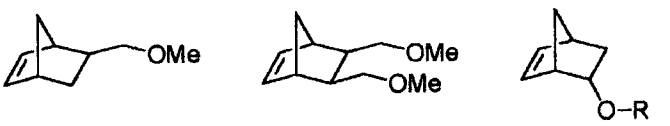

Figure 6.1. exo-5-methoxymethylnorbornene, exo,exo-5,6-bis(methoxymethyl)norbornene and endo-5-alkoxynorbornene

Subsequent molecular modelling studies of the propagating species present in these systems, revealed that the pendant oxygen functionality is in an orientation which prevents it from chelating to the ruthenium centre (*Figure 6.2a*). However the models reveal that if the oxygen atom in the 5-position is bonded directly to the norbornene backbone in an *endo*-configuration (i.e. *endo*-5-alkoxynorbornenes, *Figure 6.1*), then it may be able to chelate to the ruthenium centre (*Figure 6.2b*).

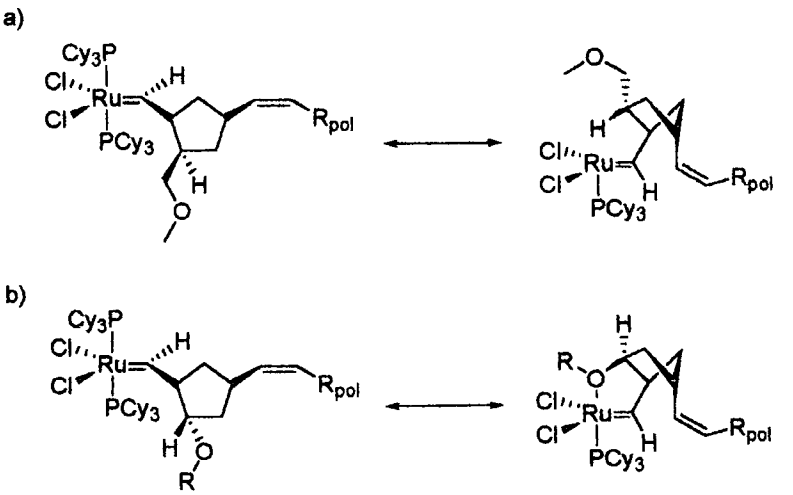

Figure 6.2. Propagating ruthenium alkylidene species of a) exo-5-methoxymethylnorbornene, and b) endo-5-alkoxynorbornenes in which oxygen is unable, and able to chelate to the metal centre, respectively

It would be interesting to prepare *endo*-5-alkoxynorbornene monomers and assess whether regeneration of the initiator, and/or oxygen chelation to the ruthenium centre is observed when they are subjected to ROMP mediated by initiator **A**.

6.2.3 Confirmation of the Identity of Species X

The identity of species X, which arises at ~17.5 ppm in ^{1}H NMR spectroscopy when 7-alkoxynorbornadiene monomers are subjected to ROMP mediated by initiator **A**, could be further confirmed by cross metathesis between initiator **A** and the corresponding functionalised cyclopentene ring (*Figure 6.3*).

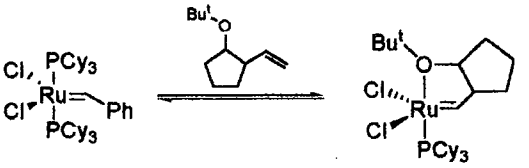

Figure 6.3. Cross metathesis resulting in an analogue of species X

6.2.4 The Synthesis of Polymers Suitable for Characterisation by MALDI-TOF Mass Spectroscopy

In order to establish whether the mechanism for regeneration of the initiator occurs via intra- and/or intermolecular secondary metathesis reactions at the propagating polymer chain-ends, further attempts to synthesise difunctional monomers should be made. Ideally, when the monomer is subjected to ROMP mediated by initiator **A**, after regeneration of the initiator has been observed, the recovered polymer should be suitable for characterisation by MALDI-TOF MS.

6.2.5 Extending Induced Regeneration of Ruthenium Complexes to RCM Systems

It would be of significant commercial interest if the phenomenon of inducing regeneration of ruthenium complexes from ROMP reactions mediated by initiator **A** could be extended into the field of RCM. The attempts to achieve this in the work reported in this thesis were impeded by the inherent lack of reactivity between the methylidene complex, $RuCl_2(PCy_3)_2(=CH_2)$, which remains at the end of an RCM reaction and acyclic olefinic terminating agents.

It is reported that $RuCl_2(PCy_3)_2(=CH_2)$ is active for RCM and ROMP.[2] When used to mediate an RCM reaction the nature of the alkylidene complex at the end of reaction remains unchanged, but when employed to perform ROMP, a substituted alkylidene species is formed (*Figure 6.4*).

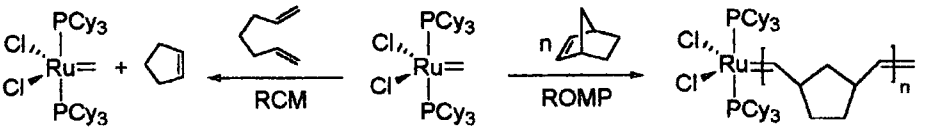

Figure 6.4. The alkylidene species formed when $RuCl_2(PCy_3)_2(=CH_2)$ is used to mediated RCM or ROMP

Therefore if, at the end of an RCM reaction, a small excess of a bicyclic monomer is added to the system, the methylidene species should perform olefin metathesis and consequently be converted into a substituted alkylidene species (*Figure 6.5*). Subsequent addition of an acyclic olefinic terminating agent should, as in the case of ROMP systems, result in the induced formation of ruthenium alkylidene complexes that can be recovered and re-used to perform olefin metathesis.

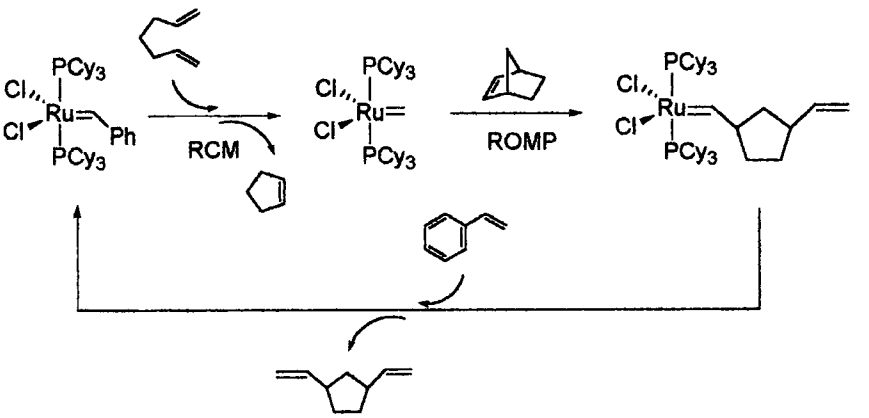

Figure 6.5. Proposed mechanism for induced regeneration of ruthenium complexes from RCM reactions via ROMP.

The main considerations that will need to be addressed if this procedure is employed, will be to minimise the loss of active ruthenium alkylidene sites during the numerous metathesis reactions required to regenerate a metathesis complex, and also the problem of the oligomeric by-products that will contaminate the RCM product.

6.2.6 Induced Regeneration of Immobilised Ruthenium Complexes

Recently, the immobilisation of olefin metathesis catalyst onto polymeric supports has received a significant amount of interest. There are four established techniques by which ruthenium species, of the type $RuX_2L_2(=CHR)$, can be attached to polymeric supports (Section 1.4.6).

The induced regeneration and recovery of ruthenium complexes from ROMP systems has been demonstrated in this thesis (Chapter 5). The major problem associated with this technique, was the recovery of the complexes from the reaction mixture once regeneration had been induced, due to the polymer and initiator both being soluble in the reaction solvent.

To overcome this problem, it is envisaged that the initiator should be attached to an insoluble support. The immobilised initiator could be used to mediate a polymerisation, and addition of a suitable terminating agent would induce regeneration of the desired supported ruthenium complex. This could then be recovered by simply filtering the reaction mixture, enabling the regenerated ruthenium complex to be recovered in high yields.

In order for this methodology to be successful, attention needs to be paid to the manner in which the ruthenium complex is attached to the support. In the case of supporting initiator **A** for use in ROMP, immobilisation via halogen exchange seems the most viable option.[3] During olefin metathesis, the halogen ligands of the ruthenium alkylidene complex remain bound to the metal centre, and therefore the active sites will remain bound to the polymeric support during the reaction. Leaching of the initiator during olefin metathesis is reported to be minimal, resulting in low levels of ruthenium contamination of the product. For ROMP using this type of support, the polymer remains immobilised during the reaction, and is cleaved by the addition of acyclic olefinic terminating agents, but the initiator remains bound to the support.

Other known techniques for supporting the initiator have their limitations. Immobilisation via the phosphine ligands results in an appreciable loss in metathesis activity and significant levels of leaching are encountered.[4,5] Supporting the initiator via alkylidene exchange, results in the polymer being grafted to the support and the initiator remaining in solution.[6]

The catalytic cycle for ROMP that could be employed if the initiator is attached to the support via halogen exchange is shown in *Figure 6.6*. Immobilisation of the initiator in this manner makes ROMP a potentially useful industrial process. If the supported complexes can be regenerated in good yields and retain their activity for use in

subsequent olefin metathesis reactions, then this technique will allow expensive non-recyclable ruthenium initiators to be employed as cost-effective re-usable catalysts.

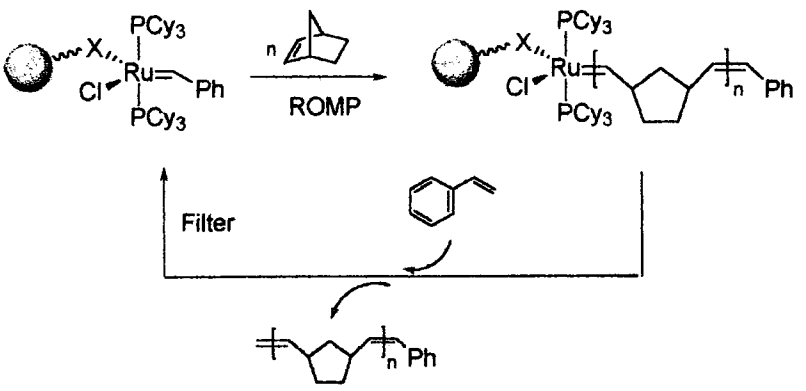

Figure 6.6. Recyclable immobilised ruthenium complexes used for ROMP

This immobilised methodology could also be applied to the technique proposed for recovering ruthenium complexes from RCM reactions (Section 6.2.5). At the end of an RCM reaction using this type of support, an immobilised ruthenium methylidene species will be present. This could be isolated from the RCM products by filtration. If it is reacted with a small excess of a bicyclic monomer followed by the addition of an acyclic terminating agent the ruthenium complex will be regenerated. The use of a supported initiator in this manner for RCM, eliminates the problem of contamination of the desired products with oligomers, and allows the initiator to be recycled.

If the techniques described above can be successfully developed to induce the regeneration of supported ruthenium complexes from RCM and ROMP systems, then it is envisaged that continuous processes of catalytic olefin metathesis systems can be set-up (*Figure 6.7*). Ideally, the systems will be finely tuned to maximise both the olefin metathesis activity of the ruthenium complexes, and the number of catalytic cycles that each system can perform. The extent of leaching of the initiator also needs to be minimised. If these factors are successfully addressed then these systems should be extremely attractive for use in commercial olefin metathesis processes.

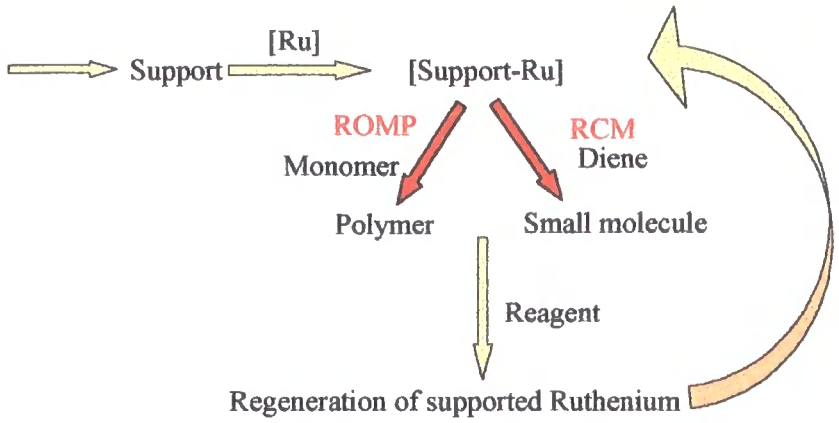

Figure 6.7. Proposed catalytic cycle for supported olefin metathesis reactions

6.3 References

1. K. J. Ivin, A. M. Kenwright, E. Khosravi, J. G. Hamilton, *Macromolecular Chemistry and Physics* **2001**, *202*, 3624.
2. P. Schwab, R. H. Grubbs, J. W. Ziller, *Journal of the American Chemical Society* **1996**, *118*, 100.
3. P. Nieczypor, W. Buchowicz, W. J. N. Meester, F. P. J. T. Rutjes, J. C. Mol, *Tetrahedron Letters* **2001**, *42*, 7103.
4. S. T. Nguyen, R. H. Grubbs, *Journal of Organometallic Chemistry* **1995**, *497*, 195.
5. K. Melis, D. De Vos, P. Jacobs, F. Verpoort, *Journal of Molecular Catalysis A: Chemical* **2001**, *169*, 47.
6. M. Ahmed, A. G. M. Barrett, D. C. Braddock, S. M. Cramp, P. A. Procopiou, *Tetrahedron Letters* **1999**, *40*, 8657.

Chapter 7

Instrumentation, Measurements and Experimental Procedures

7.1 Instrumentation and measurements

7.1.1 Nuclear Magnetic Resonance

NMR spectra were recorded on a Varian Mercury 400 or a Varian Inova 500. Typically 32 scans for ^{1}H NMR spectra were collected, and chemical shifts are quoted in ppm, relative to tetramethylsilane (0 ppm). ^{13}C NMR spectra were recorded at 100 or 125 MHz (2000 scans) using continuous broad band proton decoupling and a 3s recycle delay, and are therefore not quantitative; chemical shifts are quoted in ppm, relative to $CDCl_3$ (77.0 ppm). ^{31}P NMR spectra were obtained at 202 MHz, and typically 256 scans were collected. The NMR spectra of air-sensitive materials were recorded in tubes sealed with a Young's tap.

7.1.2 Elemental Analysis

Elemental analyses were obtained on an Exeter Analytical Inc. CE-440 elemental analyser.

7.1.3 Mass Spectrometry

Electron Impact (EI) and Electrospray (ES^{+}) mass spectra were recorded on a Micromass Autospec spectrometer operating at 70 eV with the ionisation mode as indicated.

7.1.4 Infra-red Spectroscopy

Infra-red spectra were recorded on a Perkin Elmer 1600 series FTIR. The spectra obtained were of the pure compound between sodium chloride discs.

7.1.5 Matrix Assisted Laser Desorption Ionisation Time of Flight (MALDI-TOF) Mass Spectrometry

MALDI-TOF mass spectrometry was performed using an Applied Biosystems Voyager-DE STR BioSpectrometry workstation. The samples were dissolved in the relevant solvent and premixed with the matrix, also dissolved in the relevant solvent. Spectra were obtained in either linear or reflector mode. Samples of poly(**1**) could not be characterised by MALDI-TOF MS due to insufficient ionisation to enable them to fly. The following matrices were used; 3,5-dimethoxy-4-hydoxycinnamic acid (predominantly trans), alpha-cyano-4-hydroxycinnamic acid, 2,5-dihydroxybenzoic acid, 2,4,6-trihydroxyaceophenone monohydrate, 5-chlorosalicylic acid, 9H-

pyrido[3,4-b]indole, trans-3-(3-indolyl)-acrylsaeure, 2-(4-hydroxyphenylazo)-benzoic acid (HABA), 1,8,9-trihydroxyanthracen (dithranol), all-trans-retinoic acid.

7.1.6 Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) data was obtained using a Viscotek TDA 302 equipped with 2 x 300 mm PLgel 5 μm mixed C columns. Tetrahydrofuran was used as the eluent, at a flow rate of 1.0 mL/min at 30 °C. The detectors were calibrated using polystyrene standards. This type of conventional GPC analysis, based on polystyrene standards, is unsuitable to determine actual molecular weights of poly(norbornene) derivatives, but can be used to compare relative molecular weights.[1-3]

7.2 Materials

All reagents used were of standard reagent grade and purchased from Aldrich or Lancaster and used as supplied unless otherwise stated.

$CDCl_3$ (99.9 %D, 0.03 % v/v TMS) and C_6D_6 (99.6 % D, 0.03 % v/v TMS) were dried over P_2O_5 and CaH_2 respectively, and distilled prior to use. CD_2Cl_2 (99.9 %D, 0.03 % v/v TMS) was obtained in pre-sealed ampoules. Tetrahydrofuran was dried over sodium/benzophenone and distilled prior to use. All other solvents were used without prior purification.

All liquid monomers were degassed by three freeze-thaw-pump cycles before being taken into the glove-box. Norbornene was dried over sodium and distilled under vacuum prior to use. *exo,endo*-5,6-dicarbomethoxynorbornene (**2a**),[4] *exo,exo*-5,6-dicarbomethoxynorbornene (**2b**),[5,6] *endo,endo*-5,6-dicarbomethoxynorbornene (**2c**),[4] *exo*-N-phenyl-5,6-dicarboxyimidonorbornene (**3a**),[7] and *exo*-N-phenylmethyl-5,6-dicarboxyimidonorbornene (**3b**),[7] were synthesized according to literature procedures. *cis*-2,2'-dimethoxystilbene was purchased from Specs. $RuCl_2(PPh_3)_2$(=CHPh) (**B**) was kindly provided by Materia. *exo*-5-hexylnorbornene (**13**) was kindly provided by Promerus LLC.

7.2.1 Synthesis of $RuCl_2(PCy_3)_2$(=CHPh) (A)[8]

Benzaldehyde tosylhydrazone (5 g, 18.2 mmol) and benzyltriethylammonium chloride (0.75 g, 3.29 mmol) were dissolved in hexanes (40 mL) and toluene (8 mL). A 15 wt% solution of $NaOH/H_2O$ (150 mL) was added to the reaction vessel and the mixture was heated and vigorously stirred for 2 hours at 70 °C. The mixture was

poured onto ice (100 g) and, once all of the ice had melted, the aqueous layer was discarded and the organic layer was washed with water (2 x 150 mL). The organic layer was dried over Na_2SO_4 and degassed with N_2.

$RuCl_2(PPh_3)_3$ (7.00 g, 7.3 mmol) was dissolved, with stirring, in dichloromethane (250 mL) under an inert atmosphere. The solution was cooled to -50 °C and the chilled phenyldiazomethane solution (prepared above) was added (via a polyethylene cannula) over a 15 minute period. The solution was allowed to warm to -20 °C, and tricyclohexylphosphine (4.50 g, 16.1 mmol) was added via a solid addition funnel over a 10 minute period. The resulting solution was warmed to room temperature and concentrated in vacuo, to leave a thick dark slurry. Degassed methanol (200 mL) was added with stirring, the resulting purple precipitate was collected by filtration in air, and washed with methanol (3 x 150 mL) followed by acetone (3 x 100 mL). The crude purple complex was purified by dissolution in degassed dichloromethane (30 mL) followed by filtration through celite. The solvent was removed under vacuum and methanol (150 mL) was added. The precipitate was isolated by filtration in air and washed with methanol (2 x 150 mL) followed by acetone (2 x 100 mL). The purple solid was dried under vacuum to yield 4.10 g (68 %) of $RuCl_2(PCy_3)_2(=CHPh)$.

^1H NMR (500 MHz, $CDCl_3$): δ 19.99 (s, 1H, $\mathbf{H_1}$), 8.44 (d, 2H, $\mathbf{H_3}$, J = 7.5 Hz), 7.55 (t, 1H, $\mathbf{H_5}$, J = 7.0 Hz), 7.33 (t, 2H, $\mathbf{H_4}$, J = 7.5 Hz), [2.62, 1.85-1.60, 1.50-1.35 and 1.30-1.10] (all m, $\mathbf{H_{PCy3}}$) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ 207.0 ($\mathbf{C_1}$), 152.5 ($\mathbf{C_2}$), [130.8, 129.1, 128.9 ($\mathbf{C_{3-5}}$)], [32.0, 30.9, 27.8, 26.5 ($\mathbf{C_{PCy3}}$)] ppm.

^{31}P NMR (202 MHz, $CDCl_3$): δ 36.80 ppm.

Elemental Analysis: Calc. (found) for $C_{43}H_{72}Cl_2P_2Ru$: C, 62.76 (62.20); H, 8.82 (8.81).

Mass Spec. (ES^+): *m/z* = 789.3 $[M-^{35}Cl]^+$, 787.3 $[M-^{37}Cl]^+$, 281.2 [free PCy_3].

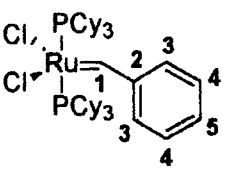

Figure 7.1. Key for NMR assignments of $RuCl_2(PCy_3)_2(=CHPh)$ (A)

7.2.2 Synthesis of $RuCl_2(PCy_3)(IMes)(=CHPh)$ (D)[9,10]

A suspension of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (5.0 g, 14.7 mmol) in tetrahydrofuran (80 mL) was stirred for 15 minutes at room temperature. Potassium *tert*-butoxide (1.75 g, 15.6 mmol) was added in a single portion. The grey solution was stirred for 20 minutes and the volatiles were removed under vacuum. The residue was extracted into warm toluene (2 x 50 mL) and filtered through celite. After removal of the solvent under vacuum, the resulting brown residue was recrystallised from hexane to obtain 3.2 g (72 %) of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene as pale browns crystals.

$RuCl_2(PCy_3)_2(=CHPh)$ (1.0 g, 1.22 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes) (375 mg, 1.23mmol) were dissolved in toluene (80 mL). The resulting orange-brown solution was stirred at room temperature for 1 hour, after which time the solvent was removed under vacuum. The residue was dissolved in hexane (40 mL) and filtered, the filtrate was cooled to -78°C. After 1 hour, the solution was filtered to obtain 0.45 g (44 %) of $RuCl_2(PCy_3)(IMes)(=CHPh)$ as purple-brown microcrystals, which were washed with cold pentane and dried under vacuum. [Product contains 8 % unreacted $RuCl_2(PCy_3)_2(=CHPh)$]

^{1}H NMR (500 MHz, $CDCl_3$): δ 19.43 (s, 1H, $\mathbf{H_1}$), 8.95 (br, 1H, $\mathbf{H_{3a}}$), 7.39 (t, 1H, $\mathbf{H_5}$, J = 7.0 Hz), 7.17 (t, 1H, $\mathbf{H_{3b}}$, J = 6.5 Hz), 7.12 (t, 2H, $\mathbf{H_4}$, J = 8.0 Hz), 7.05 (s, 2H, $\mathbf{H_{10}}$), 6.97 (s, 2H, $\mathbf{H_7}$), 6.75 (br, 1H, $\mathbf{H_{10'}}$), 5.95 (br, 1H, $\mathbf{H_{10'}}$), 2.45 (br, 6H, $\mathbf{H_{12}}$), 2.36 (s, 3H, $\mathbf{H_{13}}$), 2.19 (br, 3H, $\mathbf{H_{12'}}$), 1.96 (s, 3H, $\mathbf{H_{13'}}$), 1.92 (m, 3H, $\mathbf{H_{12'}}$), [2.21, 1.73, 1.61-1.32, 1.25, 1.10-0.79] (all m, $\mathbf{H_{PCy3}}$) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ 294.1 ($\mathbf{C_1}$), 188.6 ($\mathbf{C_6}$), 150.7 ($\mathbf{C_2}$), 138.1 ($\mathbf{C_{11}}$), 137.3 ($\mathbf{C_{11'}}$), 137.0 ($\mathbf{C_9}$), 135.7 ($\mathbf{C_{8'}}$), 135.3 ($\mathbf{C_{9'}}$), 134.4 ($\mathbf{C_8}$), 128.4 ($\mathbf{C_{10}}$), 128.0 ($\mathbf{C_{10'}}$), 127.2 ($\mathbf{C_5}$), 126.8 ($\mathbf{C_4}$), 123.6 ($\mathbf{C_7}$), 123.2 ($\mathbf{C_3}$), [30.6, 26.7, 26.0, 25.2 ($\mathbf{C_{PCy3}}$)], 20.2 ($\mathbf{C_{13}}$), 20.0 ($\mathbf{C_{13'}}$), 19.9 ($\mathbf{C_{12}}$), 18.5 ($\mathbf{C_{12'}}$) ppm.

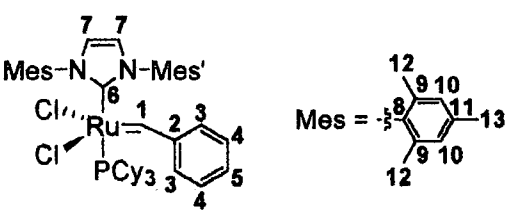

Figure 7.2. Key for NMR assignments of $RuCl_2(PCy_3)(IMes)(=CHPh)$ (D)

7.2.3 Synthesis of $RuCl_2(IMesH_2)(3\text{-}BrPyr)_2(=CHPh)$ (E)[11,12]

$RuCl_2(PCy_3)(IMesH_2)(=CHPh)$ (495 mg, 0.58 mmol) was dissolved in toluene (3 mL), and 3-bromopyridine (0.6 mL, 0.94 g, 5.96 mmol) was added. The reaction was stirred for 1 hour then cooled to -10°C. Pentane (50 mL) was added to the bright green solution, and a green solid precipitated. The precipitate was filtered, washed with pentane (2 x 20 mL), and dried under vacuum to afford 362 mg (70 %) of $RuCl_2(IMesH_2)(3\text{-}BrPyr)_2(=CHPh)$.

^1H NMR (500 MHz, $CDCl_3$): δ 19.12 (s, 1H, $\mathbf{H_1}$), 8.90-8.60 (br, 2H, $\mathbf{H_{14}}$), 8.10-7.80 (br, 2H, $\mathbf{H_{17}}$), 7.69 (d, 1H, $\mathbf{H_5}$, J = 7.5 Hz), 7.44 (t, 2H, $\mathbf{H_4}$, J = 7.5 Hz), 7.06 (t, 2H, $\mathbf{H_3}$, J = 7.5 Hz), 7.00-6.60 (br, 8H, $\mathbf{H_{10,16,18}}$), 4.09 (br, 2H, $\mathbf{H_7}$), 4.01 (br, 2H, $\mathbf{H_7}$), 2.61 (br, 6H, $\mathbf{H_{13}}$), 2.26 (br, 12H, $\mathbf{H_{12}}$) ppm.

^{13}C NMR (125 MHZ, $CDCl_3$): δ 315.7 ($\mathbf{C_1}$), 217.1 ($\mathbf{C_6}$), 152.7, 151.8, 151.4, 150.8, 148.3, 139.6, 138.8, 137.9, 135.2, 130.3, 129.4, 128.2, 124.6 ($\mathbf{C_{2\text{-}5,8\text{-}11,14\text{-}18}}$), 52.0, 51.2 ($\mathbf{C_7}$), 20.4, 18.7 ($\mathbf{C_{12,13}}$) ppm.

MS (EI): *m/z* = 107 $[IMesH_2]^+$.

Anal. Calcd. for $C_{38}H_{40}Cl_2N_4Br_2Ru$: C, 51.60; H, 4.56; N, 6.33. Found C, 51.85; H, 4.60; N, 6.13.

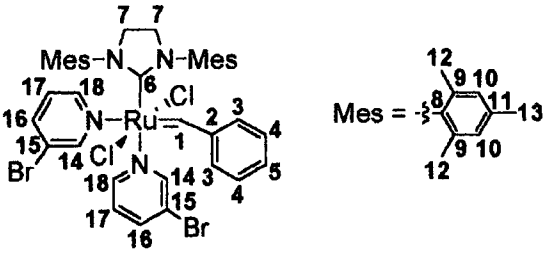

Figure 7.3. Key for NMR assignments of $RuCl_2(IMesH_2)(3\text{-}BrPyr)_2(=CHPh)$ (E)

7.2.4 Synthesis of 7-*tert*-butoxynorbornadiene (1)[13]

Norbornadiene (149 g, 1.62 mol) and cuprous bromide (0.325 g, 2.27 mmol) were dissolved in benzene (400 mL) under an inert atmosphere. The solution was stirred and heated until refluxing. *tert*-butylperoxybenzoate (122.5 g, 0.63 mol) dissolved in benzene (100 mL), was added to the solution over a period of 1 hour. After complete addition, reflux was maintained for two hours. The solution was cooled to room temperature and was washed with a 10% Na_2CO_3 solution (3 x 150 mL) and then water (3 x 150 mL). The organic layer was dried over Na_2SO_4 and filtered. Benzene was removed under vacuum. The residue was purified by reduced pressure fractional

distillation (using a 6" vigreux column) to afford 19.56 g (19 %) (63 °C / 18 mbar) of 7-*tert*-butoxynorbornadiene.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.64 (m, 2H, $\mathbf{H_{2,3}}$), 6.59 (m, 2H, $\mathbf{H_{5,6}}$) 3.78 (br s, 1H, $\mathbf{H_7}$), 3.40 (sx, 2H, $\mathbf{H_{1,4}}$, J = 2.0 Hz), 1.14 (s, 9H, $\mathbf{H_9}$) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0 ($\mathbf{C_{2,3}}$), 137.5 ($\mathbf{C_{5,6}}$), 104.5 ($\mathbf{C_7}$), 73.8 ($\mathbf{C_8}$), 55.7 ($\mathbf{C_{1,4}}$), 28.6 ($\mathbf{C_9}$) ppm.
Elemental Analysis: Calc. (found) for $C_{11}H_{16}O$: C, 80.44 (79.93); H, 9.82 (9.72).
Mass Spec. (EI): *m/z* = 164.3 $[M]^+$, 149.1 $[M\text{-}CH_3]^+$, 106.9 $[M\text{-}C(CH_3)_3]^+$, 90.9 $[M\text{-}OC(CH_3)_3]^+$.
Infra-red: wavenumber; 2974.7 (saturated C-H stretch), 1103.5 (C-O-C stretch) cm^{-1}.

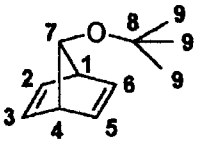

Figure 7.4. Key for NMR assignments of 7-tert-butoxynorbornadiene (1)

7.2.5 Synthesis of 7-*iso*-propoxynorbornadiene (5)

7-*tert*-butoxynorbornadiene (6.94 g, 42.3 mmol) was dissolved in propan-2-ol (50 mL) under an inert atmosphere and sulphuric acid (7 mL) dissolved in propan-2-ol (50 mL) was added drop wise with stirring. The solution was heated to 40 °C and stirred for 3 days. The reaction mixture was poured onto ice (75 g) and extracted with dichloromethane (3 x 25 mL). The combined organic layers were washed successively with saturated solutions of $NaHCO_3$ (3 x 50 mL) and NaCl (3 x 50 mL). After drying over $MgSO_4$ and filtering, the solvent was removed under vacuum and the residue was purified by fractional distillation under reduced pressure to afford 2.68 g (42 %) (52-54 °C / 18 mbar) of 7-*iso*-propoxynorbornadiene.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.64 (t, 2H, $\mathbf{H_{2,3}}$, J = 2.4 Hz), 6.56 (t, 2H, $\mathbf{H_{5,6}}$, J = 1.6 Hz), 3.70 (s, 1H, $\mathbf{H_7}$), 3.51 (m, 1H, $\mathbf{H_8}$), 3.48 (m, 2H, $\mathbf{H_{1,4}}$), 1.10 (d, 6H, $\mathbf{H_9}$, J = 6.4 Hz) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9 ($\mathbf{C_{2,3}}$), 137.4 ($\mathbf{C_{5,6}}$), 108.0 ($\mathbf{C_7}$), 70.4 ($\mathbf{C_8}$), 54.1 ($\mathbf{C_{1,4}}$), 22.7 ($\mathbf{C_9}$) ppm.
Elemental Analysis: Calc. (found) for $C_{10}H_{14}O$: C, 79.96 (79.79); H, 9.39 (9.33).

Mass Spec. (EI): *m/z* = 149.0 $[M-H]^+$, 135.0 $[M-CH_3]^+$, 106.9 $[M-CH(CH_3)_2]^+$, 91.2 $[M-O\ CH(CH_3)_2]^+$.

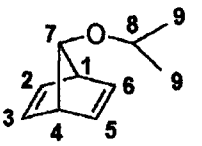

Figure 7.5. Key for NMR assignments of 7-iso-propoxynorbornadiene (5)

7.2.6 Synthesis of 7-ethoxynorbornadiene (6)

7-*tert*-butoxynorbornadiene (20.6 g, 0.125 mol) was dissolved in ethanol (200 mL) under an inert atmosphere and sulphuric acid (14 mL) was added drop wise. The solution was heated to 30 °C and stirred for 5 hours. The reaction mixture was poured onto ice (150 g) and extracted with dichloromethane (4 x 25 mL). The combined organic layers were washed successively with saturated solutions of $NaHCO_3$ (3 x 50 mL) and NaCl (3 x 50 mL). After drying over $MgSO_4$ and filtering, the solvent was removed under vacuum and the residue was purified by fractional distillation under reduced pressure to afford 2.75 g (16 %) (48-50 °C / 18 mbar) of 7-ethoxynorbornadiene.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (m, 2H, $\mathbf{H_{2,3}}$), 6.57 (m, 2H, $\mathbf{H_{5,6}}$), 3.65 (m, 1H, $\mathbf{H_7}$), 3.52 (m, 2H, $\mathbf{H_{1,4}}$), 3.37 (q, 2H, $\mathbf{H_8}$, J = 7.2 Hz), 1.13 (t, 3H, $\mathbf{H_9}$, J = 7.2 Hz) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1 ($\mathbf{C_{2,3}}$), 137.3 ($\mathbf{C_{5,6}}$), 109.1 ($\mathbf{C_7}$), 64.0 ($\mathbf{C_8}$), 53.1 ($\mathbf{C_{1,4}}$), 28.5 ($\mathbf{C_9}$) ppm.
Elemental Analysis: Calc. (found) for $C_9H_{12}O$: C, 79.37 (97.21); H, 8.88 (8.63).
Mass Spec. (EI): *m/z* = 136.0 $[M]^+$, 106.9 $[M-CH_2CH_3]^+$, 91.3 $[M-OCH_2CH_3]^+$.

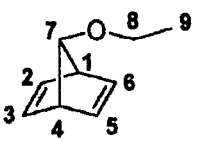

Figure 7.6. Key for NMR assignments of 7-ethoxynorbornadiene (6)

7.2.7 Synthesis of 7-methoxynorbornadiene (7)[14]

Concentrated sulphuric acid (8 mL) was added drop wise to a stirred solution of 7-*tert*-butoxynorbornadiene (12.90 g, 78.5 mmol) in methanol (120 mL). The reaction

mixture was heated to 30 °C and stirred for 5 hours. The solution was poured onto ice (100 g) and extracted with dichloromethane (4 x 20 mL). The combined extracts were washed successively with saturated solutions of $NaHCO_3$ (3 x 30 mL) and NaCl (3 x 30 mL). The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed under vacuum and the residue was purified by reduced pressure fractional distillation (using a 6" vigreux column) to afford 4.42 g (46 %) (40-42 °C / 18 mbar) of 7-methoxynorbornadiene.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.65 (m, 2H, $\mathbf{H_{2,3}}$), 6.59 (m, 2H, $\mathbf{H_{5,6}}$), 3.59 (m, 1H, $\mathbf{H_7}$), 3.56 (m, 2H, $\mathbf{H_{1,4}}$), 3.22 (s, 3H, $\mathbf{H_8}$) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3 ($\mathbf{C_{2,3}}$), 137.5 ($\mathbf{C_{5,6}}$), 110.3 ($\mathbf{C_7}$), 56.6 ($\mathbf{C_8}$), 52.8 ($\mathbf{C_{1,4}}$) ppm.
Elemental Analysis: Calc. (found) for $C_8H_{10}O$: C, 78.65 (78.36); H, 8.25 (8.12).
Mass Spec. (EI): m/z = 122.0 $[M]^+$, 107.0 $[M\text{-}CH_3]^+$,91.0 $[M\text{-}OCH_3]^+$.

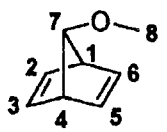

Figure 7.7. Key for NMR assignments of 7-methoxynorbornadiene (7)

7.2.8 Synthesis of *exo*-5-methoxymethylnorbornene (8)

Under an inert atmosphere, *exo*-5-methanolnorbornene (3.20 g, 25.8 mmol) dissolved in dry tetrahydrofuran (10 mL) was added drop wise to a stirred solution of NaH (0.77 g, 32.2 mmol) in dry tetrahydrofuran (30 mL). After complete addition, the solution was stirred for 30 minutes. Methyl iodide (9.14 g, 64.4 mmol) was added drop wise to the solution and a slight exotherm was observed. The reaction was stirred at room temperature for 2 hours. Water (~5 mL) was added drop wise to quench any remaining NaH. The solution was poured onto diethylether (250 mL) and filtered. It was then washed with water (4 x 100 mL) and dried over $MgSO_4$. After filtration, the solvent was removed under vacuum to yield the crude product (3.88 g) as a yellow oil. The residue was purified by fractional distillation under reduced pressure to afford 1.81 g (51 %) (68-72 °C / 45 mbar) of *exo*-5-methoxymethylnorbornene.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.10 (dd, 1H, $\mathbf{H_3}$, J = 5.6, 2.8 Hz), 6.05 (dd, 1H, $\mathbf{H_2}$, J = 5.6, 2.8 Hz), 3.42 (dd, 1H, $\mathbf{H_{6'}}$, J = 9.2, 6.4 Hz), 3.36 (s, 3H, $\mathbf{H_9}$), 3.29 (t, 1H, $\mathbf{H_6}$, J

= 8.8 Hz), 2.80 (br. s, 1H, $\mathbf{H_4}$), 2.73 (br. s, 1H, $\mathbf{H_1}$), 1.68 (m, 1H, $\mathbf{H_5}$), 1.31 (q, 2H, $\mathbf{H_8}$, J = 4.4 Hz), 1.24 (dt, 1H, $\mathbf{H_7}$, J = 11.6, 2.0 Hz), 1.11 (dt, 1H, $\mathbf{H_{7'}}$, J = 11.6, 4.0 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8(2) ($\mathbf{C_3}$), 136.8(0) ($\mathbf{C_2}$), 77.8 ($\mathbf{C_8}$), 59.0 ($\mathbf{C_9}$), 45.2 ($\mathbf{C_6}$), 43.9 ($\mathbf{C_5}$), 41.7 ($\mathbf{C_4}$), 39.1 ($\mathbf{C_1}$), 29.9 ($\mathbf{C_7}$) ppm.

Elemental Analysis: Calc. (found) for $C_9H_{14}O$: C, 78.21 (77.83); H, 10.21 (10.04).

Mass Spec. (EI): *m/z* = 138.0 $[M]^+$, 123.0 $[M\text{-}CH_3]^+$, 107.0 $[M\text{-}OCH_3]^+$, 90.9 $[M\text{-}CH_2OCH_3]^+$.

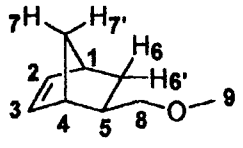

Figure 7.8. Key for NMR assignments of exo-5-methoxymethylnorbornene (8)

7.2.9 Synthesis of *exo,exo*-5,6-bis(methoxymethyl)norbornene (9)[15]

Under an inert atmosphere, *exo,exo*-5,6-dicarbinolnorbornene (5.00 g, 32.4 mmol) was dissolved in dry tetrahydrofuran (10 mL) and was added drop wise to a stirred solution of NaH (1.94 g, 80.8 mmol) dissolved in dry tetrahydrofuran (30 mL). After complete addition the solution was stirred for 30 minutes. Methyl iodide (22.11 g, 155.8 mmol) was added drop wise, a slight exotherm was observed and the solution became less viscous. The solution was stirred at room temperature for 2 hours. Water (~5 mL) was added drop wise to quench any remaining NaH, and the white precipitate dissolved. The solution was poured onto diethylether (250 mL) and filtered (slight ppt. observed). The mixture was washed with water (4 x 100 mL) and dried over $MgSO_4$. After filtration, the solvent was removed under vacuum to yield the crude product as a yellow oil. The residue was purified by reduced pressure fractional distillation to afford 3.76 g (64 %) (29-32 °C / 8 x 10^{-2} mbar) of *exo,exo*-5,6-bis(methoxymethyl)norbornene.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14 (t, 2H, $\mathbf{H_{2,3}}$, J = 1.6 Hz), 3.52 (dd, 2H, $\mathbf{H_{8,10}}$, J = 8.8, 4.4 Hz), 3.34 (s, 6H, $\mathbf{H_{9,11}}$), 3.25 (t, 2H, $\mathbf{H_{8,10}}$, J = 8.4 Hz), 2.74 (m, 2H, $\mathbf{H_{1,4}}$), 1.77 (m, 2H, $\mathbf{H_{5,6}}$), 1.47 (d, 1H, $\mathbf{H_7}$, J = 8.8 Hz), 1.29 (dt, 1H, $\mathbf{H_{7'}}$, J = 8.8, 1.6 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3 ($\mathbf{C_{2,3}}$), 74.1 ($\mathbf{C_{8,10}}$), 58.7 ($\mathbf{C_{9,11}}$), 44.7 ($\mathbf{C_{5,6}}$), 42.6 ($\mathbf{C_{1,4}}$), 40.5 ($\mathbf{C_7}$) ppm.

Elemental Analysis: Calc. (found) for $C_{11}H_{18}O_2$: C, 72.49 (71.80); H, 9.95 (9.86).
Mass Spec. (EI): *m/z* =182.1 $[M]^+$, 151.1 $[M\text{-}OCH_3]^+$, 137.1 $[M\text{-}CH_2OCH_3]^+$.

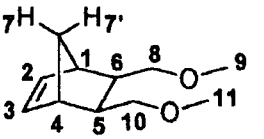

Figure 7.9. Key for NMR assignments of exo,exo-5,6-bis(methoxymethyl)norbornene (9)

7.2.10 Synthesis of 7-acetoxynorbornadiene (10)[13]

7-*tert*-butoxynorbornadiene (15 g, 91.3 mmol) was added to a mixture of glacial acetic acid (150 mL) and acetic anhydride (30 mL). The solution was allowed to stand at room temperature for 30 minutes. It was then cooled in an ice-bath and quickly added to 70 % perchloric acid (20.3 g, 141 mmol) which had been previously cooled to 0 °C. The deep red mixture was swirled and allowed to stand in the ice-bath for 1 minute. The solution was poured into a separating funnel containing ice and water (500 mL). The product was extracted with dichloromethane (4 x 50 mL). The combined organic layers were washed with saturated $NaHCO_3$ (3 x 50 mL), water (3 x 50 mL), saturated NaCl (3 x 50 mL) and dried over $MgSO_4$. After removal of the volatiles, distillation under reduced pressure afforded 7.62 g (56 %) (61 °C / 10.5 mbar) of 7-acetoxynorbornadiene.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (t, 2H, $\mathbf{H_{2,3}}$, J = 2.4 Hz), 6.58 (m, 2H, $\mathbf{H_{5,6}}$), 4.57 (m, 1H, $\mathbf{H_7}$), 3.60 (m, 2H, $\mathbf{H_{1,4}}$), 1.98 (s, 3H, $\mathbf{H_9}$) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0 ($\mathbf{C_8}$), 140.3 ($\mathbf{C_{2,3}}$), 137.8 ($\mathbf{C_{5,6}}$), 99.3 ($\mathbf{C_7}$), 52.4 ($\mathbf{C_{1,4}}$), 21.1 ($\mathbf{C_9}$) ppm.
Elemental Analysis: Calc. (found) for $C_9H_{10}O_2$: C,71.98 (71.70); H, 6.71 (6.72).
Mass Spec. (EI): *m/z* = 150.18 $[M]^+$, 108.0 $[M\text{-}(C{=}O)CH_3]^+$, 91.0 $[M\text{-}O(C{=}O)CH_3]^+$.
Infra-red: wavenumber; 2988.4 (saturated C-H stretch), 1737.0 (C=O stretch), 1245.1 (C-O-C=O stretch) cm^{-1}.

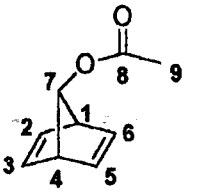

Figure 7.10. Key for NMR assignments of 7-acetoxynorbornadiene (10)

7.2.11 Synthesis of 7-hydroxynorbornadiene (11)[13]

A Grignard reagent was prepared by the drop wise addition of methyl iodide (21.84 g, 0.154 mol) to magnesium turnings (4.31 g, 0.177 mol) in anhydrous diethylether (100 mL) under a nitrogen atmosphere at 0 °C. Once addition was complete, the solution was heated at reflux for 30 minutes and then cooled to room temperature. 7-acetoxynorbornadiene (7.62 g, 0.051 mol) in diethylether (100 mL) was added drop wise over a 15-minute period. After addition, the reaction was allowed to stir at room temperature for 1 hour. Water (100 mL) and Na_2SO_4 (10 g) were added and the ether was decanted. The remaining salts were washed thoroughly with diethylether (4 x 50 mL). The ether extracts were combined, washed with water (3 x 100 mL) and dried over $MgSO_4$. After careful removal of the ether, and the product distilled under reduced pressure to afford 2.18 g (40 %) (71-73 °C / 75 mbar) of 7-hydroxynorbornadiene. The alcohol was further purified by column chromatography on silica gel (1:1 petroleum ether: diethylether).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.66 (m, 2H, $\mathbf{H_{2,3}}$), 6.61 (m, 2H, $\mathbf{H_{5,6}}$), 3.88 (d, 1H, $\mathbf{H_7}$, J = 12.8 Hz), 3.47 (m, 2H, $\mathbf{H_{1,4}}$), 3.11 (d, 1H, $\mathbf{H_8}$, J = 13.2 Hz, OH – disappears upon addition of D_2O) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0 ($\mathbf{C_{2,3}}$), 138.2 ($\mathbf{C_{5,6}}$), 102.3 ($\mathbf{C_7}$), 56.1 ($\mathbf{C_{1,4}}$) ppm.

Elemental Analysis: Calc. (found) for C_7H_8O: C, 77.75 (76.63); H, 7.46 (7.52).

Mass Spec. (EI): *m/z* = 108.0 $[M]^+$, 91.0 $[M\text{-}OH]^+$.

Infra-red: wavenumber; 3404.7 (broad, O-H stretch), 2987.0 (saturated C-H stretch) cm^{-1}.

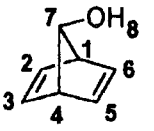

Figure 7.11. Key for NMR assignments of 7-hydroxynorbornadiene (11)

7.2.12 Synthesis of 7-neopentylnorbornadiene (12a)

Under a nitrogen atmosphere, anhydrous diethylether (80 mL) was transferred into an oven-dried two-necked round bottom flask containing magnesium turnings (3.07 g, 0.126 mol). The flask was cooled in an ice-bath, and neopentyl iodide (23.85 g, 0.120 mol) was added drop wise with stirring over a 30 minute period. The solution was

refluxed for 30 minutes. Benzene (80 mL) was added to the solution in four portions (4 x 20 mL) and the ether was removed by distillation. The solution was cooled to room temperature, and 7-*tert*-butoxynorbornadiene (10.60g, 0.065 mol) was added. The reaction was heated at reflux under nitrogen for 4 days. After cooling to room temperature, water (30 mL) was added drop wise to destroy any remaining Grignard reagent. The resulting magnesium residue was solubilised by addition of 50 % HCl (30 mL). The benzene layer was separated and washed with 10 % Na_2CO_3 solution (3 x 100 mL) followed by water (3 x 100 mL), it was then dried over Na_2SO_4. After filtration, the benzene was removed under vacuum. The residue was purified by reduced pressure fractional distillation to afford 6.1 g (46-54 °C / 18 mbar) of a mixture of unreacted 7-*tert*-butoxynorbornadiene and 7-neopentylnorbornadiene. These were separated by column chromatography (12:1 petroleum ether/ethyl acetate) to yield 0.74 g (7.1 %) of 7-neopentylnorbornadiene.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.81 (m, 2H, $\mathbf{H_{2,3}}$), 6.58 (m, 2H, $\mathbf{H_{5,6}}$), 3.33 (m, 2H, $\mathbf{H_{1,4}}$), 2.57 (t, 1H, $\mathbf{H_7}$, J = 6.4 Hz), 1.24 (d, 2H, $\mathbf{H_8}$, J = 6.4 Hz), 0.83 (s, 9H, $\mathbf{H_{10}}$) ppm.
^{13}C NMR (125 MHz, $CDCl_3$): δ 144.8 ($\mathbf{C_{2,3}}$), 140.3 ($\mathbf{C_{5,6}}$), 84.7 ($\mathbf{C_7}$), 55.4 ($\mathbf{C_8}$), 43.9 ($\mathbf{C_{1,4}}$), 30.6 ($\mathbf{C_9}$), 29.9 ($\mathbf{C_{10}}$) ppm.
Elemental Analysis: Calc. (found) for $C_{12}H_{18}$: C, 88.82 (87.63); H, 11.18 (10.96).
Mass Spec. (EI): *m/z* = 162.0 $[M]^+$, 147.0 $[M\text{-}CH_3]^+$, 104.6 $[M\text{-}C(CH_3)_3]^+$, 90.9 $[M\text{-}CH_2C(CH_3)_3]^+$.

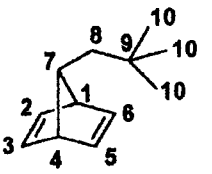

Figure 7.12. Key for NMR assignments of 7-neopentylnorbornadiene (12a)

7.2.13 Synthesis of 7-ethylnorbornadiene (12b)

By the same procedure as 7-neopentylnorbornadiene, 7-ethylnorbornadiene was prepared by the Grignard reaction between magnesium turnings (5.84 g, 0.240 mol), ethyl iodide (37.58 g, 0.242 mol) and 7-*tert*-butoxynorbornadiene (18.60 g, 0.113 mol). After removal of benzene under vacuum, the residue was purified by reduced pressure fractional distillation to afford 2.05 g (24-28 °C / 18 mbar) of a crude oil.

This was passed through a column of silica (1:1 dichloromethane/hexane) to yield 0.85 g (6.3 %) of 7-ethylnorbornadiene.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (t, 2H, $\mathbf{H_{2,3}}$, J = 2.0 Hz)), 6.56 (t, 2H, $\mathbf{H_{5,6}}$, J = 0.8 Hz), 3.33 (m, 2H, $\mathbf{H_{1,4}}$), 2.43 (t, 1H, $\mathbf{H_7}$, J = 7.2 Hz), 1.30 (m, 2H, $\mathbf{H_8}$), 0.74 (t, 3H, $\mathbf{H_9}$, J = 7.2 Hz) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8 ($\mathbf{C_{2,3}}$), 139.9 ($\mathbf{C_{5,6}}$), 89.3 ($\mathbf{C_7}$), 53.3 ($\mathbf{C_8}$), 22.6 ($\mathbf{C_{1,4}}$), 12.3 ($\mathbf{C_9}$) ppm.
Elemental Analysis: Calc. (found) for C_9H_{12}: C, 89.93 (88.91); H, 10.06 (10.06).
Mass Spec. (EI): *m/z* = 120.0 $[M]^+$, 105.0 $[M\text{-}CH_3]^+$, 91.0 $[M\text{-}CH_2CH_3]^+$.

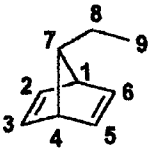

*Figure 7.13 Key for NMR assignments of 7-ethylnorbornadiene (**12b**)*

7.2.14 Synthesis of 7-methylnorbornadiene (12c)[16]

A Grignard reaction between magnesium turnings (5.84 g, 0.240 mol), methyl iodide (34.2g, 0.241mol) and 7-*tert*-butoxynorbornadiene (18.64g, 0.113mol) was employed to prepare 7-methylnorbornadiene. After removal of benzene under vacuum, the residue was purified by fractional distillation under atmospheric pressure to yield 0.80 g (6.7 %) (b.p. 78-80°C) of 80:20 7-methylnorbornadiene/benzene.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (s, C_6H_6), 6.80 (m, 2H, $\mathbf{H_{2,3}}$), 6.56 (m, 2H, $\mathbf{H_{5,6}}$), 3.24 (m, 2H, $\mathbf{H_{1,4}}$), 2.64 (q, 1H, $\mathbf{H_7}$, J = 6.0 Hz), 0.87 (d, 3H, $\mathbf{H_8}$, J = 6.0 Hz) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9 ($\mathbf{C_{2,3}}$), 139.9 ($\mathbf{C_{5,6}}$), 128.3 (C_6H_6), 81.6 ($\mathbf{C_7}$), 55.4 ($\mathbf{C_{1,4}}$), 15.4 ($\mathbf{C_8}$) ppm.
Elemental Analysis: Calc. (found) for C_8H_{10}: C, 90.51 (89.29); H, 9.49 (9.33).
Mass Spec. (EI): *m/z* = 106.1 $[M]^+$, 91.0 $[M\text{-}CH_3]^+$.

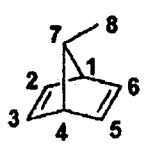

*Figure 7.14 Key for NMR assignments of 7-methylnorbornadiene (**12c**)*

7.2.15 Synthesis of 2-*iso*-propoxybenzaldehyde[17]

Salicylaldehyde (15.15 g, 124.1 mmol) was added to a suspension of K_2CO_3 (34.22 g, 0.248 mol) in dimethylformamide (200 mL). 2-bromopropane (15.20 g, 0.124 mol) was added drop wise and the solution was stirred at room temperature for 21 hours. After the addition of water (200 mL), the mixture was extracted with diethylether (3 × 150 mL). The combined organic extracts were washed with 2M NaOH (3 × 100 mL), and the organic layer was dried over $MgSO_4$. After filtration, concentration under reduced pressure yielded 8.04 g (40 %) of crude 2-*iso*-propoxybenzaldehyde, which was used in subsequent reactions without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.50 (s, 1H, $\mathbf{H_8}$), 7.83 (dd, 1H, $\mathbf{H_6}$, J = 8.0 and 2.0 Hz) 7.52 (td, 1H, $\mathbf{H_5}$, J = 8.4 and 5.6 Hz), 6.98 (m, 2H, $\mathbf{H_{3,4}}$), 4.69 (sept., 1H, $\mathbf{H_9}$, J = 6.0 Hz), 1.40 (d, 6H, $\mathbf{H_{10}}$, J = 6.0 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5 ($\mathbf{C_7}$), 160.84 ($\mathbf{C_1}$), [136.0, 128.5, 125.9, 120.6, 114.2] ($\mathbf{C_{2\text{-}6}}$), 71.3 ($\mathbf{C_9}$), 22.2 ($\mathbf{C_{10}}$) ppm.

Elemental Analysis: Calc. (found) for $C_{10}H_{12}O_2$: C, 73.15 (69.51); H, 7.37 (7.07).

Mass Spec. (EI): *m/z* = 164.2 $[M]^+$, 135.0 $[M\text{-}(C{=}O)H]^+$, 120.9 $[M\text{-}OCH(CH_3)_2]^+$.

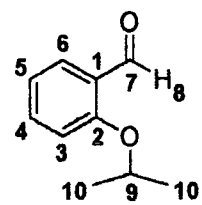

Figure 7.15 Key for NMR assignments of 2-iso-propoxybenzaldehyde

7.2.16 Synthesis of 2-*iso*-propoxystyrene[18]

Under an inert atmosphere, methyltriphenylphosphonium bromide (17.47 g, 48.9 mmol) was dissolved in diethylether (100 mL) in a 3-neck RBF fitted with a reflux condenser and a mechanical stirrer. n-Butyllithium (1.6 M, 30.46 mL, 48.7 mmol) in hexanes was added drop wise, and the mixture stirred for 4 hours. 2-*iso*-propoxybenzaldehyde (8.00 g, 48.7 mmol) in diethylether (40 mL) was added drop wise causing the precipitation of a white solid. The reaction mixture was heated at reflux for 18 hours. The resulting suspension was filtered and the filtrate was concentrated under vacuum. The crude product was purified by silica gel

chromatography (9:1 40/60 petroleum ether: ethyl acetate) to yield 3.8 g (48 %) of 2-*iso*-propoxystyrene.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (dd, 1H, **H_3**, J = 7.6, 1.6 Hz), 7.19 (td, 1H, **H_6**, J = 6.8, 1.6 Hz), 7.06 (dd, 1H, **H_7**, J = 18.0, 11.2 Hz), 6.89 (m, 2H, **$H_{4,5}$**), 5.72 (dd, 1H, **$H_{8'}$**, J = 17.6, 1.6 Hz), 5.22 (dd, 1H, **H_8**, J = 10.8, 1.6 Hz), 4.52 (sept., 1H, **H_9**, J = 6.0 Hz), 1.34 (d, 6H, **H_{10}**, J = 6.0 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2 (**C_1**), [132.1, 128.7, 128.0, 126.6, 120.6, 114.3, 113.9] (**$C_{2\text{-}8}$**), 70.9 (**C_9**), 22.2 (**C_{10}**) ppm.

Elemental Analysis: Calc. (found) for $C_{11}H_{14}O$: C, 81.44 (81.37); H, 8.70 (8.75).

Mass Spec. (EI): *m/z* = 162.0 $[M]^+$, 146.9 $[M\text{-}CH_3]^+$, 119.0 $[M\text{-}CH(CH_3)_2]^+$, 103.0 $[M\text{-}OCH(CH_3)_2]^+$.

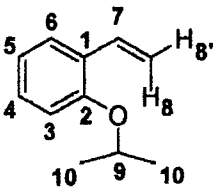

Figure 7.16 Key for NMR assignments of 2-iso-propoxystyrene

7.2.17 Attempted Synthesis of *exo*-N-phenyl-5,6-dicarboxyimido-7-*tert*-butoxynorbornene

exo-N-phenyl-5,6-dicarboxyimidonorbornene (3.2 g, 13.3 mmol) and cuprous bromide (3.0 mg, 21.0 μmol) were dissolved in benzene (50 mL) under a nitrogen atmosphere. The solution was stirred and heated until refluxing. Over a period of one hour, *tert*-butylperoxybenzoate (1.00 g, 5.15 mmol) dissolved in benzene (10 mL), was added to the solution. Reflux was maintained for 15 hours. The solution was cooled to room temperature. It was washed with a 10% Na_2SO_4 (3 x 40 mL) and then water (3 x 40 mL). The organic layer was dried over Na_2SO_4 and filtered. Benzene was removed in *vacuo* and the yellow residue was recrystallised from ethyl actetate to yield a white powder (2.4 g). ^{1}H NMR spectroscopy revealed that this compound is predominantly starting material.

7.2.18 Attempted Synthesis of *exo*-5,6-dicarboxyanhydride-7-*tert*-butoxynorbornene

exo-5,6-dicarboxyanhydridenorbornene (4.0 g, 24.4 mmol) and cuprous bromide (4.0 mg, 27.9 μmol) were dissolved in benzene (50 mL) under a nitrogen atmosphere. The

solution was stirred and heated until refluxing. Over a period of one hour, *tert*-butylperoxybenzoate (2.37 g, 12.2 mmol) dissolved in benzene (10 mL), was added to the solution. Reflux was maintained for 3 hours. The solution was cooled to room temperature. It was washed with a 10% Na_2CO_3 (3 x 40 mL) and then water (3 x 40 mL). The organic layer was dried over Na_2SO_4 and filtered. Benzene was removed in *vacuo* to yield a crude pale yellow powder (3.55 g). ^1H NMR spectroscopy revealed that the recovered material was predominantly starting material.

7.3 Experimental Procedures

7.3.1 NMR Scale ROMP Reactions

All ROMP reactions were prepared in a Braun glove box under an inert atmosphere. Typically, the relevant ruthenium complex (10 mg) was dissolved in deuterated solvent (0.4 mL) and stirred for 5 minutes. The relevant monomer (n equivalents) dissolved in deuterated solvent (0.4 mL) was added to the initiator solution and stirred for 5 minutes. The solution was transferred to an NMR tube fitted with a Young's tap, allowing the vessel to be closed under a nitrogen atmosphere. The reactions were monitored by ^1H NMR spectroscopy every 15 minutes for the first 3 hours and then at longer periods until no further reaction was observed. In all cases, the integrated intensities of the alkylidene signals were compared to that of the TMS signal, which was assumed to remain constant throughout each experiment.

In systems where free phosphines or phosphine scavengers were employed, PCy_3 or CuCl, (in 0.1 mL $CDCl_3$), respectively, was added either a) to the ruthenium complex 10 minutes prior to initiation of ROMP, or b) upon completion of the ROMP reaction. In the latter instance, the NMR tube was returned to the glove-box before addition.

7.3.2 NMR Scale Ring-Closing Metathesis Reactions

RCM reactions were prepared in a Braun glove box under an inert atmosphere. The relevant ruthenium complex (10 mg) was dissolved in $CDCl_3$ (0.4 mL) and stirred for 5 minutes. Diethyl diallylmalonate (20 equivalents) in $CDCl_3$ (0.4 mL) was added to the initiator solution. The solution was transferred to an NMR tube fitted with a Young's tap. The reactions were monitored by ^1H NMR spectroscopy.

Terminating agents were introduced to these systems in the same manner as for the NMR scale ROMP systems described in Section 6.3.1.

7.3.3 NMR Scale Cross-Metathesis Reactions

These types of reaction were prepared in a Braun glove box under an inert atmosphere. $RuCl_2(PCy_3)_2(=CHPh)$ (**A**) (10 mg) was dissolved in $CDCl_3$ (0.8 mL) and stirred for 5 minutes. The relevant amount of acyclic olefin was weighed in a vial, to which the initiator solution was added. The solution was transferred to an NMR tube fitted with a Young's tap, which allowed the vessel to be closed under a nitrogen atmosphere. The reactions were monitored by ^1H NMR spectroscopy.

7.3.4 Blockcopolymerisation of a 7-alkoxy and a 7-alkyl Norbornadiene

$RuCl_2(PCy_3)_2(=CHPh)$ (**A**) (10.1 mg, 12.2 μmol) was dissolved in $CDCl_3$ (0.2 mL). 7-neopentylnorbornadiene (**12a**) (101.1 mg, 0.62 mmol, 51.3 equivalents) was dissolved in $CDCl_3$ (0.6 mL) and was added to the initiator solution drop wise over a 10 minute period. The solution was transferred to an NMR tube fitted with a Young's tap. After obtaining a ^1H NMR spectrum, the tube was taken back into the glove-box, and 7-*tert*-butoxynorbornadiene (**1**) (49.9 mg, 0.30 mmol, 25.0 equivalents) dissolved in $CDCl_3$ (0.2 mL) was added to the reaction mixture. The reaction was monitored by ^1H NMR spectroscopy.

7.3.5 Monitoring the Molecular Weight of Poly(1) as a Function of Time

$RuCl_2(PCy_3)_2(=CHPh)$ (**A**) (0.505 mg, 0.61 mmol) was dissolved in chloroform (20 mL) and stirred for 5 minutes. 7-*tert*-butoxynorbornadiene (**1**) (5.00 g, 30.4 mmol) was dissolved in chloroform (20 mL). The monomer solution was added to the initiator solution and stirred. At various intervals, aliquots (0.4 mL) were taken from the solution and quenched with 5 drops of ethyl vinyl ether. The solvent was removed and the polymer submitted for GPC analysis.

7.3.6 Regeneration and Recovery of Initiator A

$RuCl_2(PCy_3)_2(=CHPh)$ (**A**) (203.2 mg, 0.25 mmol) was dissolved in chloroform (8.0 mL). *exo,endo*-5,6-dicarbomethoxynorbornene (**2a**) (1.02 g, 4.86 mmol) was dissolved in chloroform (8.0 mL). The monomer solution was added to the initiator solution and stirred for 5.5 hours. Styrene (52.9 mg, 0.51 mmol) in chloroform (0.5 mL) was added and the solution was stirred for 45 minutes. After removal of the

volatiles under vacuum, acetone (60 mL, -78°C) was added and the solution stirred for 10 minutes. After filtration, the residue was subjected to another acetone wash. The recovered purple solid was dried under vacuum to yield 76 mg (37 %) of recovered $RuCl_2(PCy_3)_2(=CHPh)$ (**A**). The volatiles were removed from the filtrate under vacuum to yield poly(*exo,endo*-5,6-dicarbomethoxynorbornene), which was re-precipitated into hexanes (M_n = 2,926, PDI = 1.10). $[M]_o/[I]_o$ = 19.68, $[styrene]_o/[I]_o$ = 2.06.

7.3.6.1 ROMP using Recovered Initiator A

Recovered $RuCl_2(PCy_3)_2(=CHPh)$ (**A**) (10.1 mg, 12.3 μmol) was dissolved in $CDCl_3$ (0.4 mL) and stirred for 5 minutes. *exo,endo*-5,6-dicarbomethoxynorbornene (**2a**) (51.4 mg, 0.24 mmol) was dissolved in $CDCl_3$ (0.4 mL). The monomer solution was added to the initiator solution and stirred for 5 minutes. The solution was transferred to a young's NMR tube. The reaction was monitored by ^1H NMR spectroscopy. Once the monomer had been consumed (5 hours), ethyl vinyl ether (5 drops) was added to terminate the propagating polymer chains. The polymer was recovered by precipitation into hexanes (M_n = 3,472, PDI = 1.12). $[M]_o/[I]_o$ = 19.81.

7.3.6.2 RCM using Recovered Initiator A

Recovered $RuCl_2(PCy_3)_2(=CHPh)$ (**A**) (10.4 mg, 12.6 μmol) was dissolved in $CDCl_3$ (0.4 mL). Diethyl diallylmalonate (60.6 mg, 0.25 mmol) was dissolved in $CDCl_3$ (0.4 mL). The monomer solution was added to the initiator solution and stirred for 5 minutes. The solution was transferred to a young's NMR tube. The reaction was monitored by ^1H NMR spectroscopy. $[M]_o/[I]_o$ = 19.96.

7.3.7 Formation and Recovery of Initiator F

$RuCl_2(PCy_3)_2(=CHPh)$ (**A**) (200.3 mg, 0.25 mmol) was dissolved in chloroform (8.0 mL). *exo,endo*-5,6-dicarbomethoxynorbornene (**2a**) (1.0g, 4.86 mmol) was dissolved in chloroform (8.0 mL). The monomer solution was added to the initiator solution and stirred for 5 hours. 2-*iso*-propoxystyrene (79.3 mg, 0.49 mmol) in chloroform (0.5 mL) was added and the solution was stirred for 4 hours. The volume of the solution was reduced to ~ 6 mL, and it was then added drop wise with stirring to hexanes (80 mL). After filtration of the precipitated polymer, the filtrate was evaporated to dryness under vacuum to yield 114.3 mg (77 %) of $RuCl_2(PCy_3)(=CH-$

o-O-*i*-PrC$_6$H$_4$) (**F**). The polymer was precipitated into hexanes and recovered (M_n = 2,632, PDI = 1.20). $[M]_o/[I]_o$= 19.67, [2-*iso*-propoxystyrene]$_o/[I]_o$= 1.98.

7.3.7.1 ROMP using Recovered Initiator F

Recovered $RuCl_2(PCy_3)$(=CH-*o*-O-*i*-PrC$_6$H$_4$) (**F**) (10.0 mg, 16.7 μmol) was dissolved in $CDCl_3$ (0.4 mL) and stirred for 5 minutes. *exo,endo*-5,6-dicarbomethoxynorbornene (**2a**) (70.7 mg, 0.34 mmol) was dissolved in $CDCl_3$ (0.4 mL). The monomer solution was added to the initiator solution and stirred for 5 minutes. The solution was transferred to a young's NMR tube. The reaction was monitored by ^{1}H NMR spectroscopy. Once the monomer had been consumed (9 hours), ethyl vinyl ether (5 drops) was added to terminate the propagating polymer chains and the polymer was recovered by precipitation into hexanes (M_n = 4,040, PDI = 1.32). $[M]_o/[I]_o$ = 20.20.

7.3.7.2 RCM using Recovered Initiator F

Recovered $RuCl_2(PCy_3)$(=CH-*o*-O-*i*-PrC$_6$H$_4$) (**F**) (10.1 mg, 16.8 μmol) was dissolved in $CDCl_3$ (0.4 mL) and stirred for 5 minutes. Diethyl diallylmalonate (80.6 mg, 0.34 mmol) was dissolved in $CDCl_3$ (0.4 mL). The monomer solution was added to the initiator solution and stirred for 5 minutes. The solution was transferred to a young's NMR tube and the reaction was monitored by ^{1}H NMR spectroscopy. $[M]_o/[I]_o$ = 19.95.

7.4 References

1. L. R. Gilliom, R. H. Grubbs, *Journal of the American Chemical Society* **1986**, *108*, 733.
2. T. J. Katz, S. J. Lee, N. Acton, *Tetrahedron Letters* **1976**, 4247.
3. T. J. Katz, N. Acton, *Tetrahedron Letters* **1976**, 4251.
4. W. J. Feast, J. L. Hesselink, E. Khosravi, S. P. Rannard, *Polymer Bulletin* **2002**, *49*, 135.
5. R. D. Miller, D. L. Dolce, V. Y. Merritt, *Journal of Organic Chemistry* **1976**, *41*, 1221.
6. K. F. Castner, N. Calderon, *Journal of Molecular Catalysis* **1982**, *15*, 47.
7. E. Khosravi, A. A. Al-Hajaji, *European Polymer Journal* **1998**, *34*, 153.
8. P. Schwab, R. H. Grubbs, J. W. Ziller, *Journal of the American Chemical Society* **1996**, *118*, 100.

9. A. J. Arduengo, III, H. V. R. Dias, R. L. Harlow, M. Kline, *Journal of the American Chemical Society* **1992**, *114*, 5530.
10. J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *Journal of the American Chemical Society* **1999**, *121*, 2674.
11. A. Love Jennifer, P. Morgan John, M. Trnka Tina, H. Grubbs Robert, *Angewandte Chemie International ed. in English* **2002**, *41*, 4035.
12. M. S. Sanford, J. A. Love, R. H. Grubbs, *Organometallics* **2001**, *20*, 5314.
13. P. R. Story, *Journal of Organic Chemistry* **1961**, *26*, 287.
14. R. K. Lustgarten, H. G. Richey, Jr., *Journal of the American Chemical Society* **1974**, *96*, 6393.
15. D. M. Lynn, S. Kanaoka, R. H. Grubbs, *Journal of the American Chemical Society* **1996**, *118*, 784.
16. P. R. Story, S. R. Fahrenholtz, *Journal of Organic Chemistry* **1963**, *28*, 1716.
17. R. Leardini, H. McNab, M. Minozzi, D. Nanni, D. Reed, A. G. Wright, *Journal of the Chemical Society, Perkin Transactions 1* **2001**, 2704.
18. F. Hollywood, H. Suschitzky, R. Hull, *Synthesis* **1982**, 662.

Appendix

Analytical Data

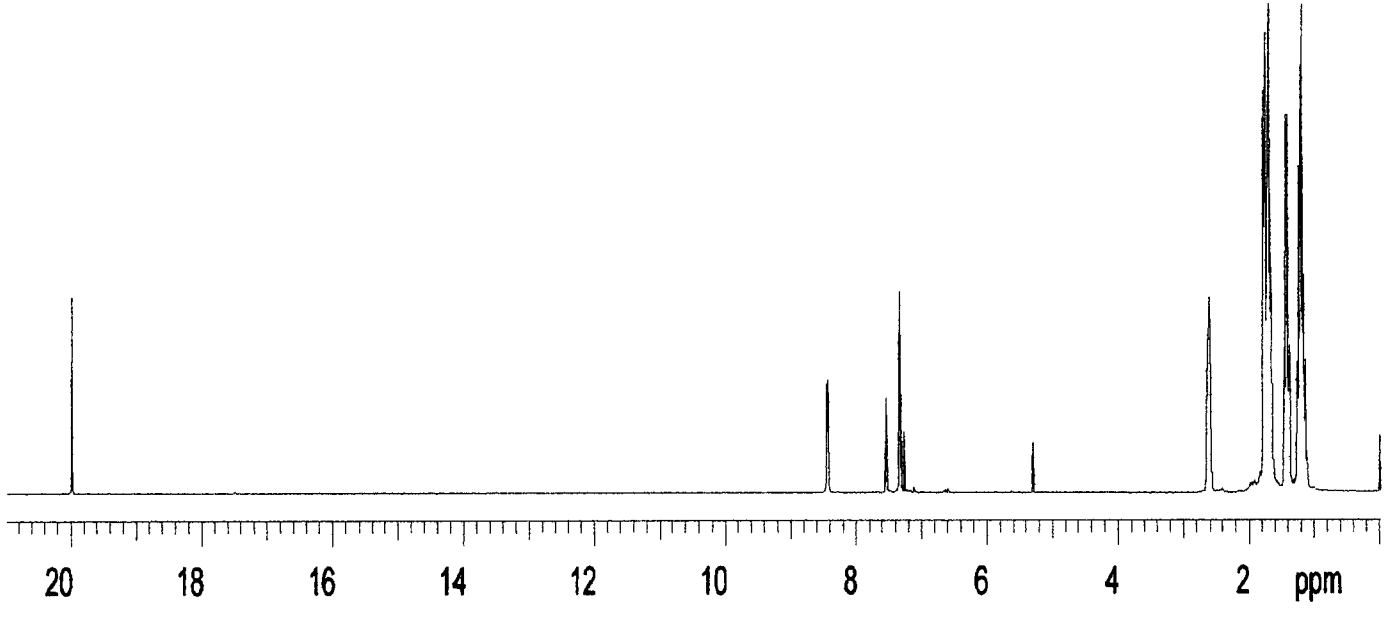

Figure A.1. ^{1}H *NMR spectrum* ($CDCl_3$) *of ruthenium,dichloro(phenylmethylene)bis(tricyclohexylphosphine)* [$RuCl_2(PCy_3)_2(=CHPh)$] **(A)**

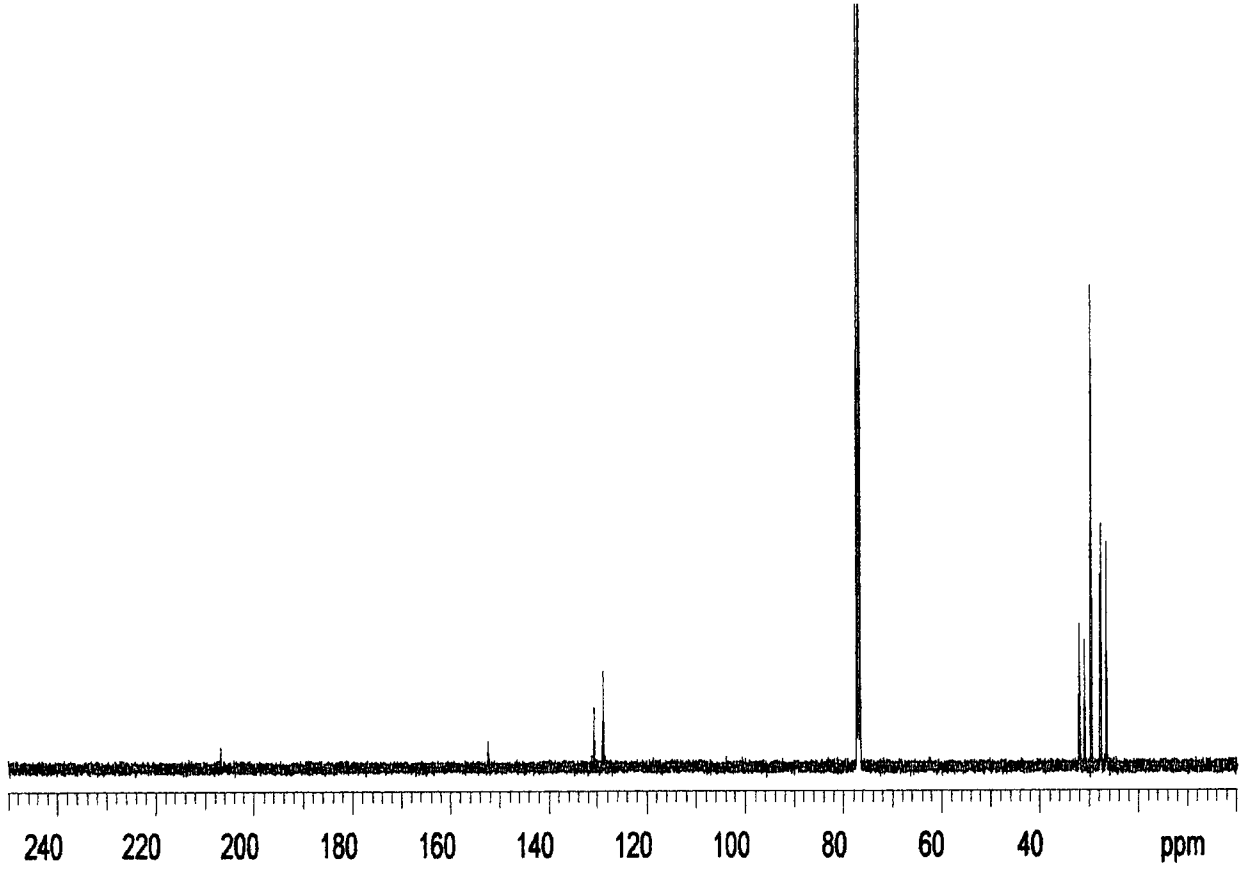

Figure A.2. ^{13}C *NMR spectrum* ($CDCl_3$) *of ruthenium,dichloro(phenylmethylene)bis(tricyclohexylphosphine)* [$RuCl_2(PCy_3)_2(=CHPh)$] **(A)**

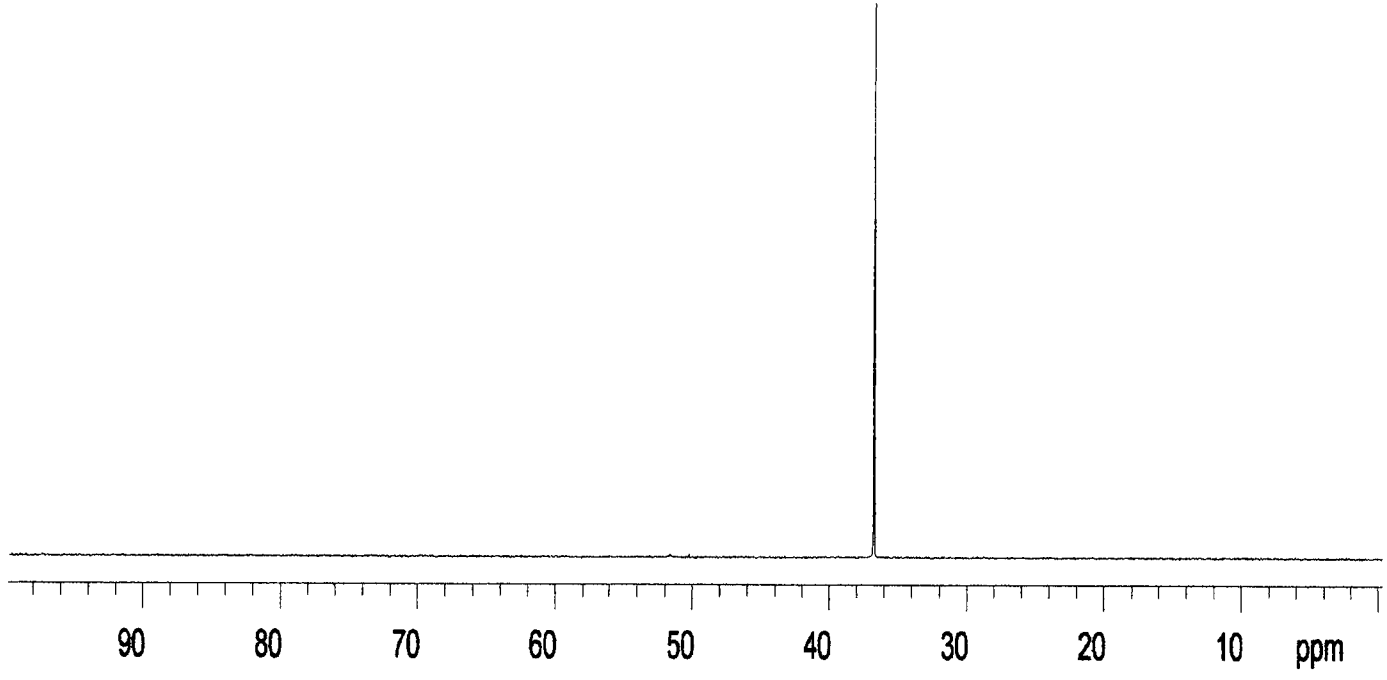

Figure A.3. ^{31}P *NMR spectrum* ($CDCl_3$) *of ruthenium,dichloro(phenylmethylene)bis(tricyclohexylphosphine)* [$RuCl_2(PCy_3)_2(=CHPh)$] **(A)**

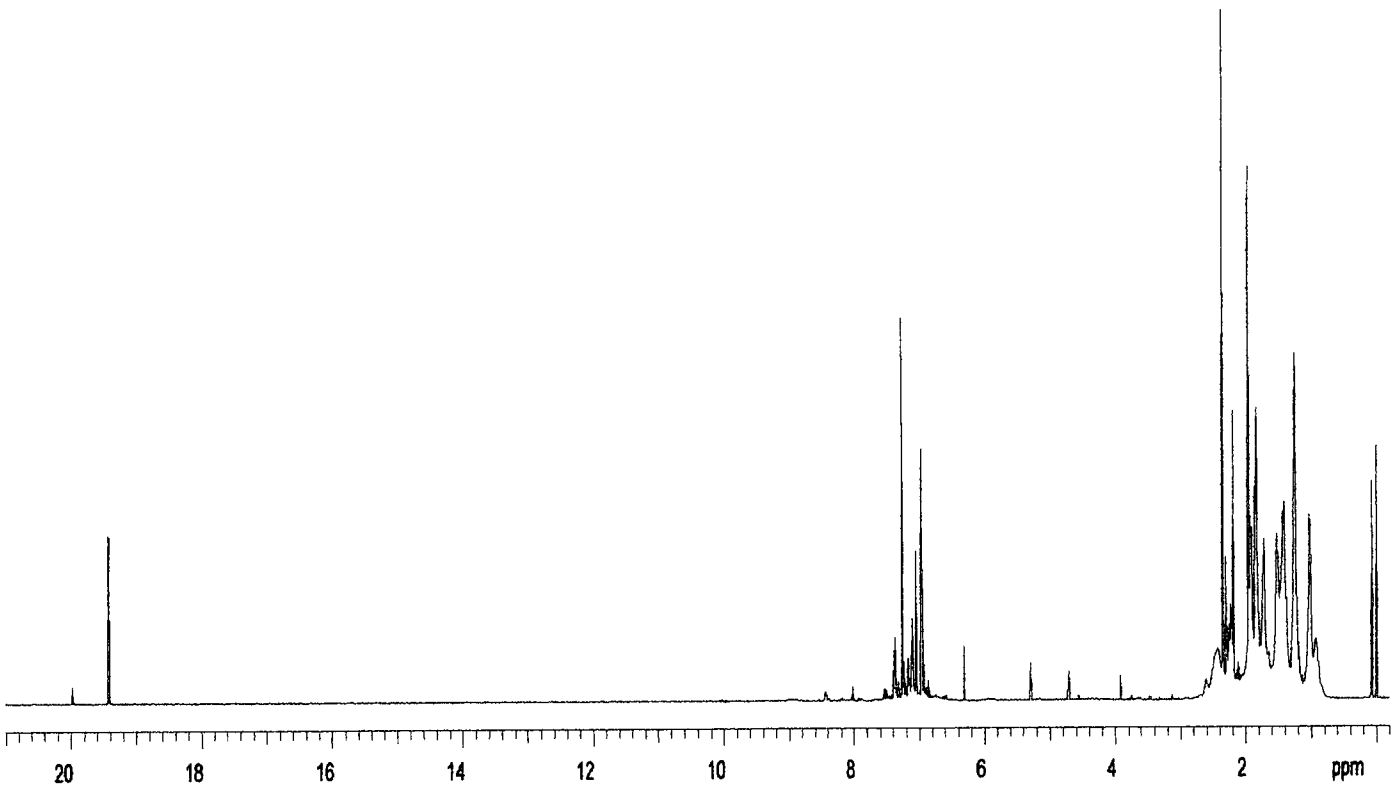

Figure A.4. ^{1}H *NMR spectrum* ($CDCl_3$) *of ruthenium[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]dichloro(phenylmethylene)(tricyclohexylphosphine)* [$RuCl_2(PCy_3)(IMes)(=CHPh)$] (**D**)

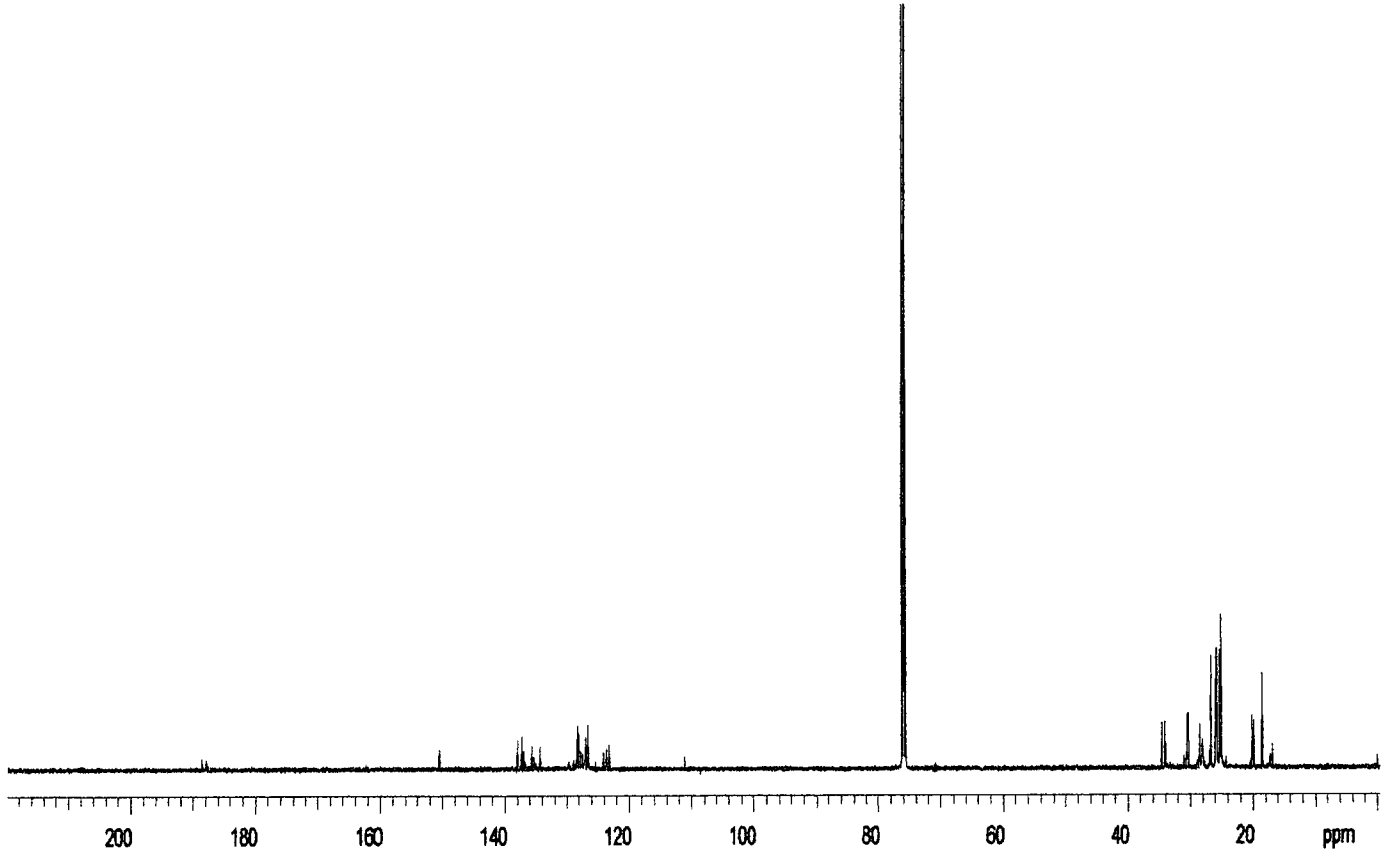

Figure A.5. ^{13}C *NMR spectrum* ($CDCl_3$) *of ruthenium[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]dichloro(phenylmethylene)(tricyclohexylphosphine)* [$RuCl_2(PCy_3)(IMes)(=CHPh)$] (**D**)

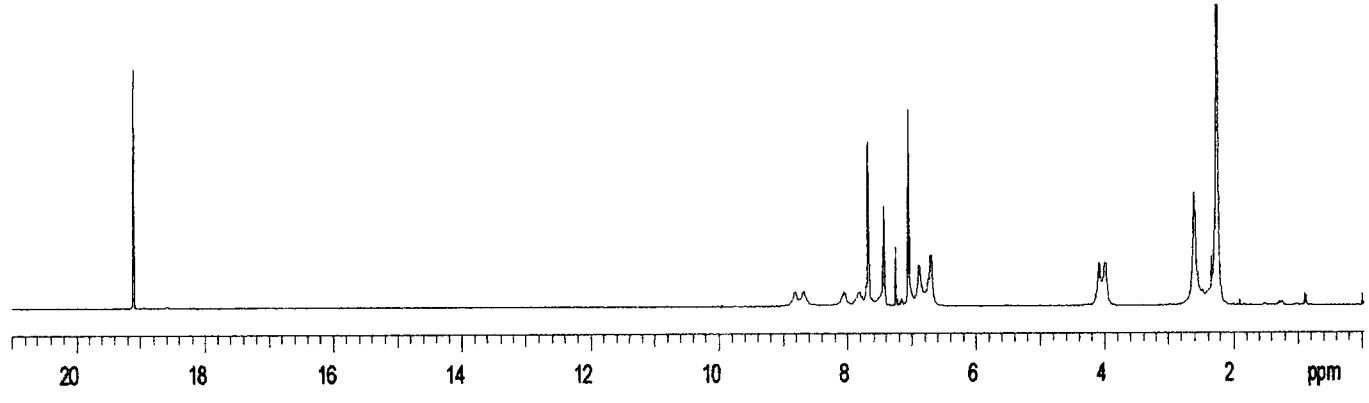

*Figure A.6. ^{1}H NMR spectrum ($CDCl_3$) of ruthenium[1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(phenylmethylene)bis(3-bromopyridene) [$RuCl_2(IMesH_2)(3\text{-}BrPyr)_2(=CHPh)$] (**E**)*

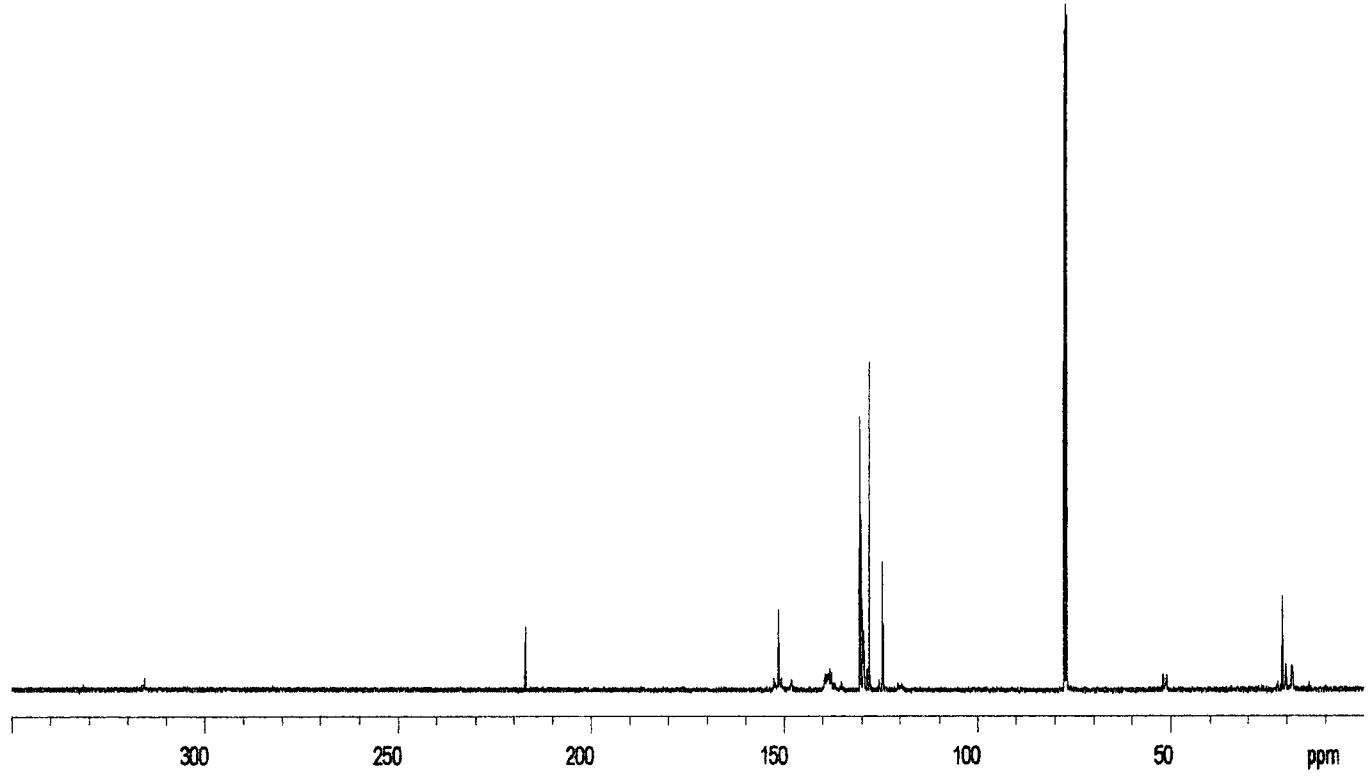

Figure A.7. ^{13}C *NMR spectrum* ($CDCl_3$) *of ruthenium[1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(phenylmethylene)bis(3-bromopyridene)* [$RuCl_2(IMesH_2)(3\text{-}BrPyr)_2(=CHPh)$] (**E**)

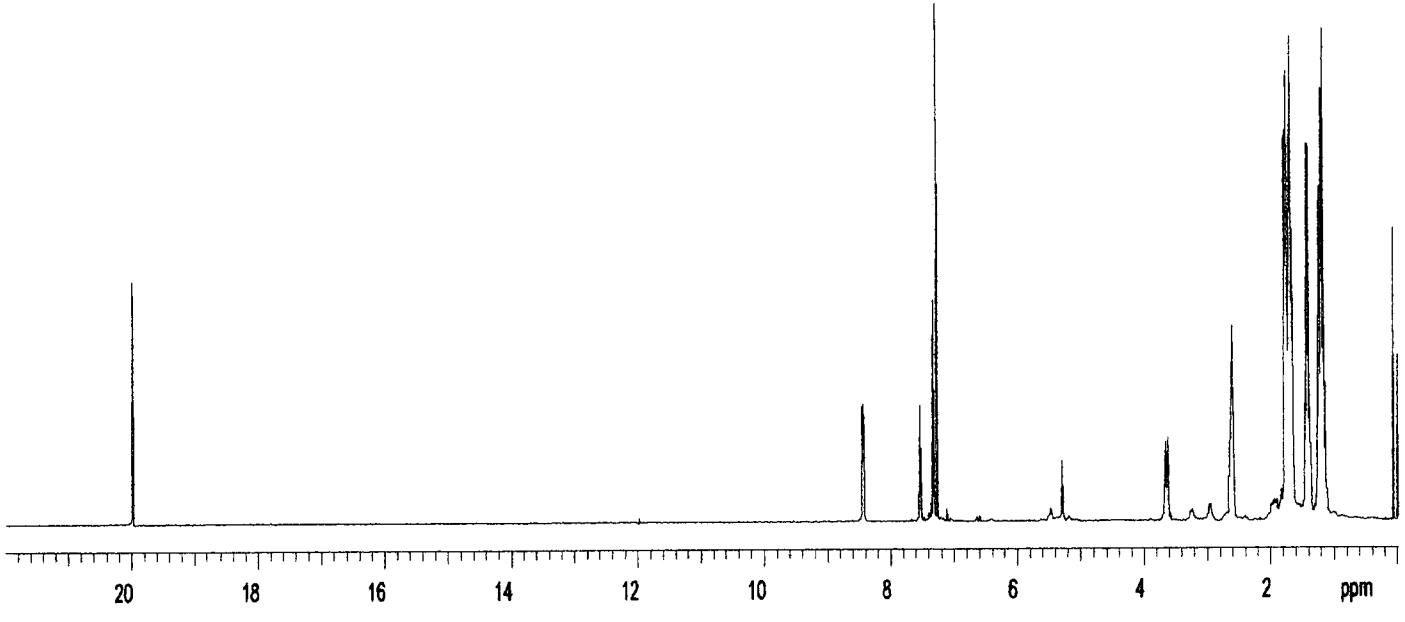

Figure A.8. ^{1}H *NMR spectrum* ($CDCl_3$) *of recovered ruthenium,dichloro(phenylmethylene) bis(tricyclohexylphosphine)* $[RuCl_2(PCy_3)_2(=CHPh)]$ ***(A)***

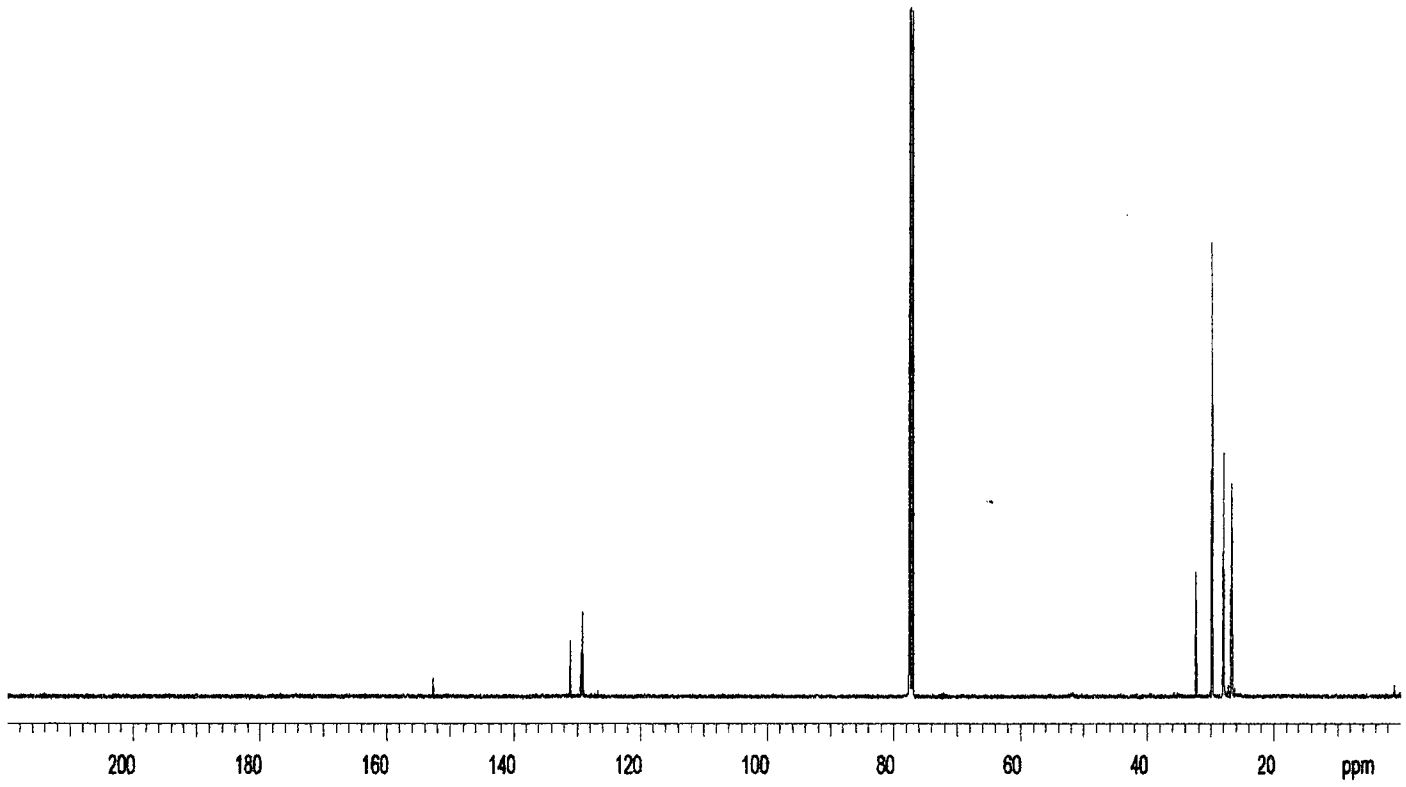

*Figure A.9. ^{13}C NMR spectrum ($CDCl_3$) of recovered ruthenium,dichloro(phenylmethylene) bis(tricyclohexylphosphine) [$RuCl_2(PCy_3)_2(=CHPh)$] (**A**)*

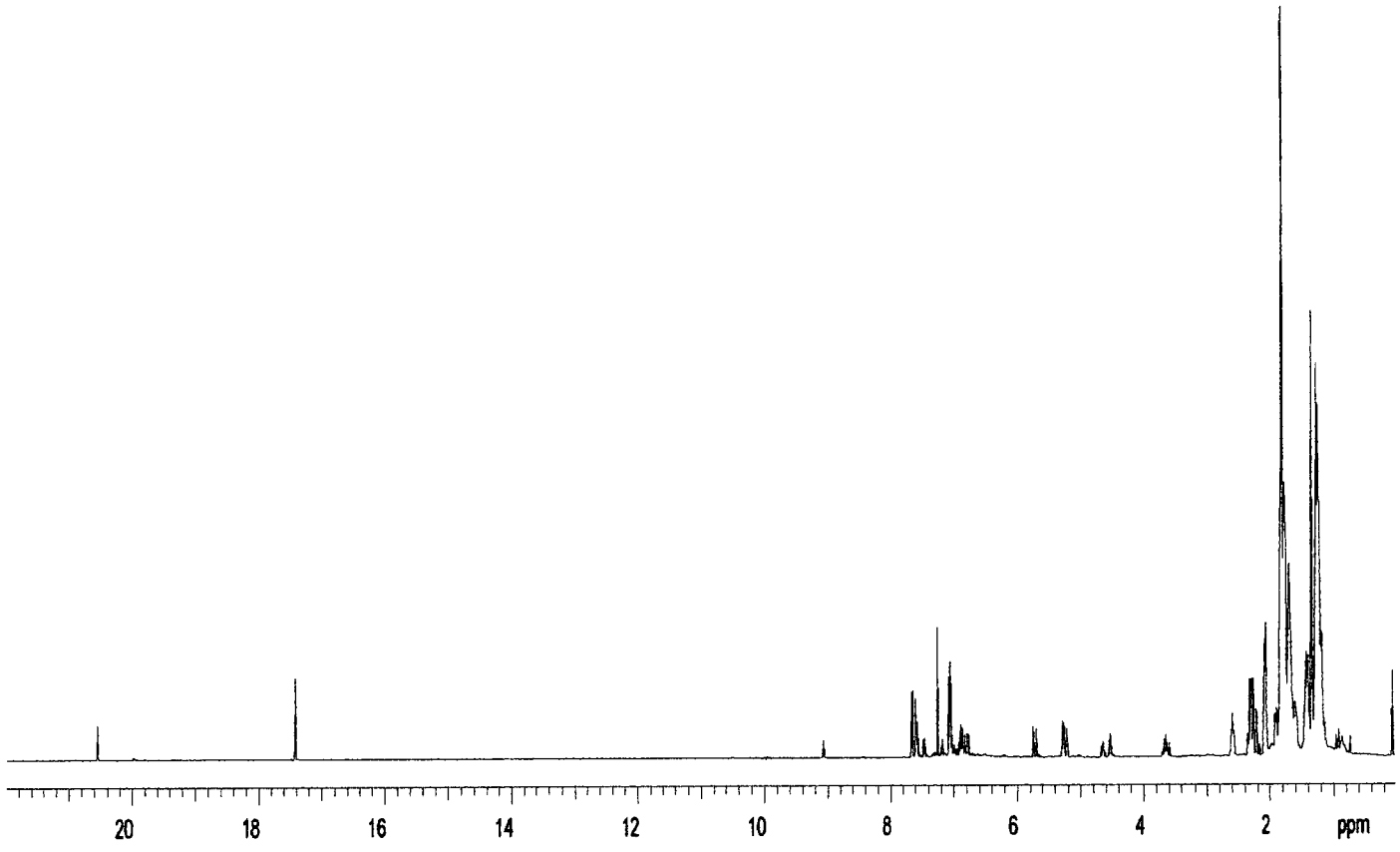

Figure A.10. ^{1}H *NMR spectrum* ($CDCl_3$) *of recovered ruthenium,dichloro[[2-(1-methylethoxy)phenyl] methylene](tricyclohexylphosphine)* $[RuCl_2(PCy_3)_2(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)]$ **(F)**

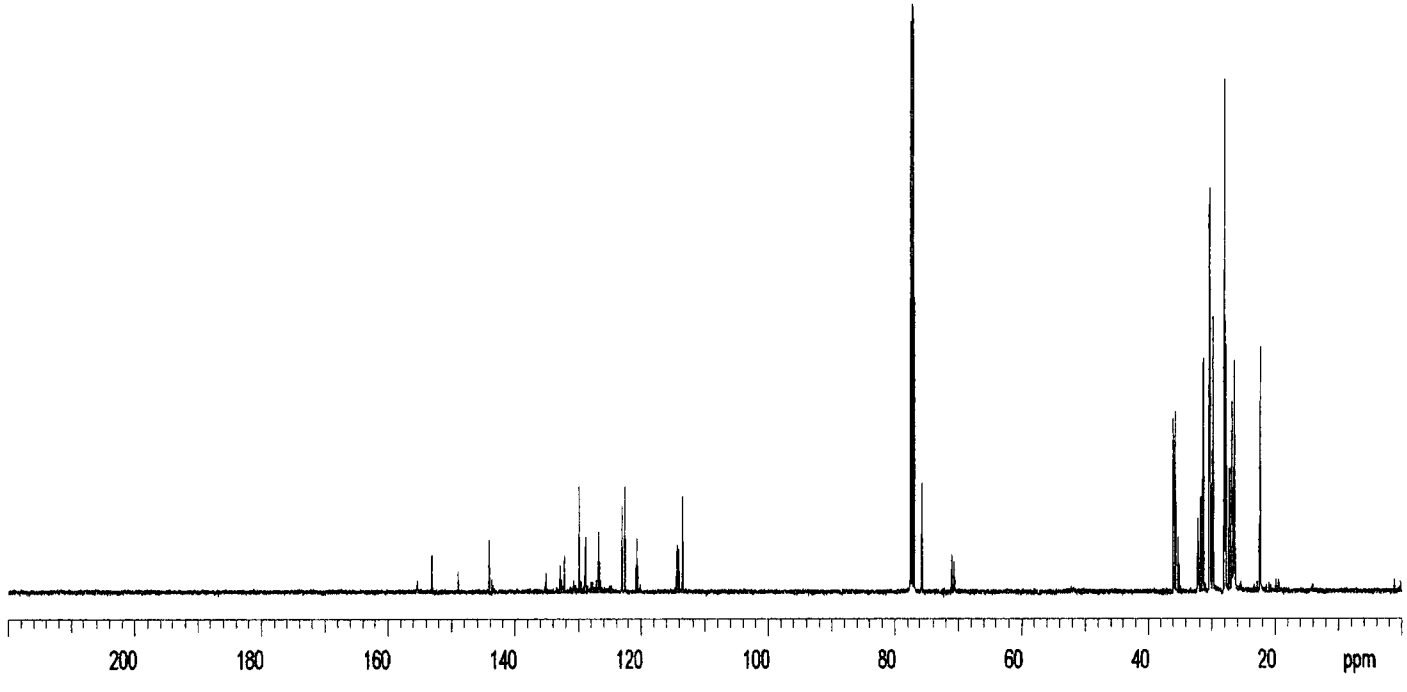

Figure A.11. ^{13}C *NMR spectrum* ($CDCl_3$) *of recovered ruthenium,dichloro[[2-(1-methylethoxy)phenyl]methylene] (tricyclohexylphosphine)* $[RuCl_2(PCy_3)_2(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)]$ ***(F)***

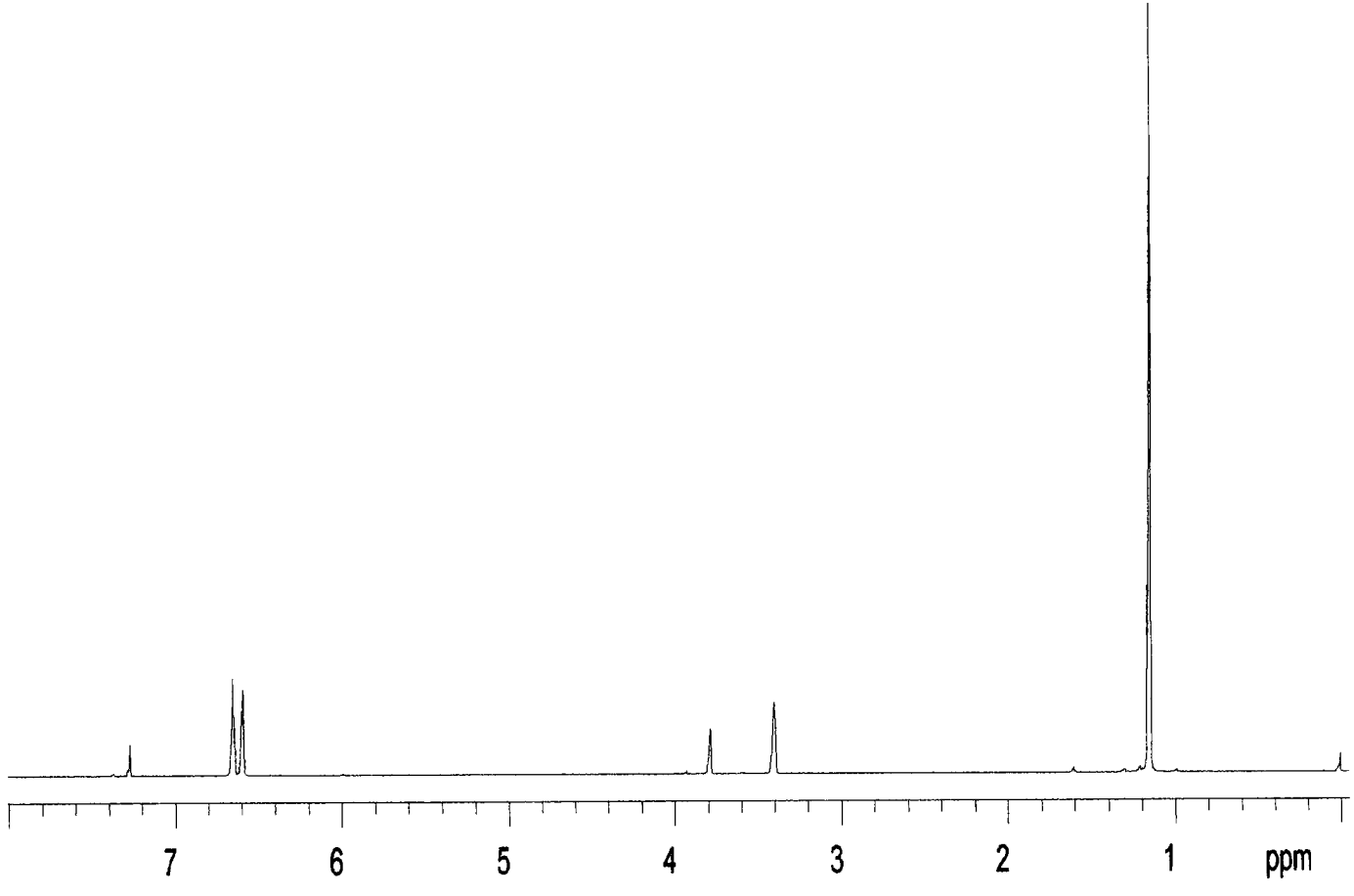

Figure A.12. ^{1}H *NMR spectrum* ($CDCl_3$) *of 7-tert-butoxynorbornadiene (**1**)*

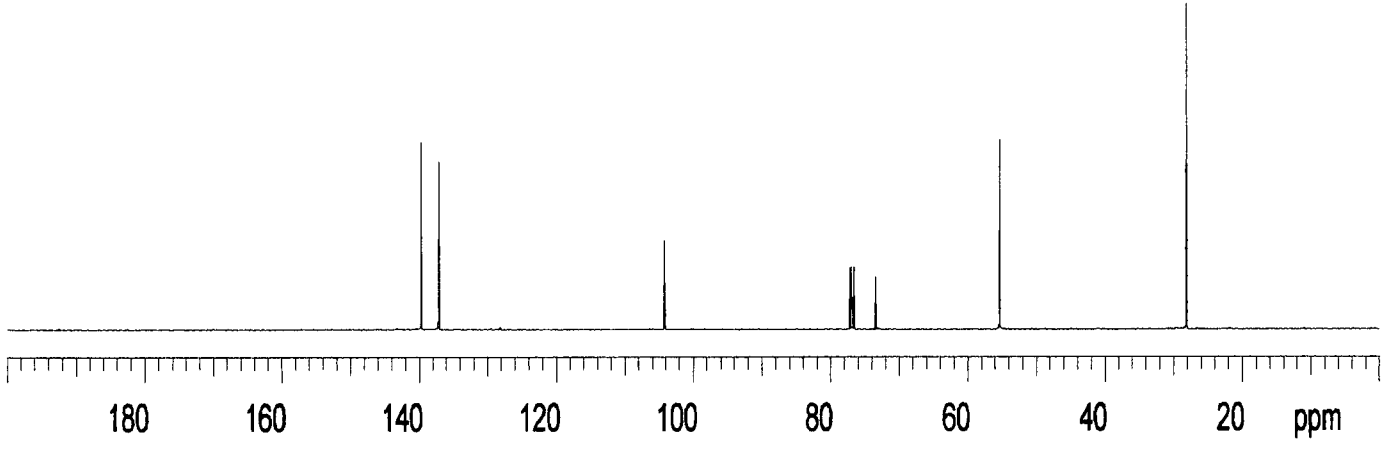

Figure A.13. ^{13}C *NMR spectrum* ($CDCl_3$) *of 7-tert-butoxynorbornadiene* (**1**)

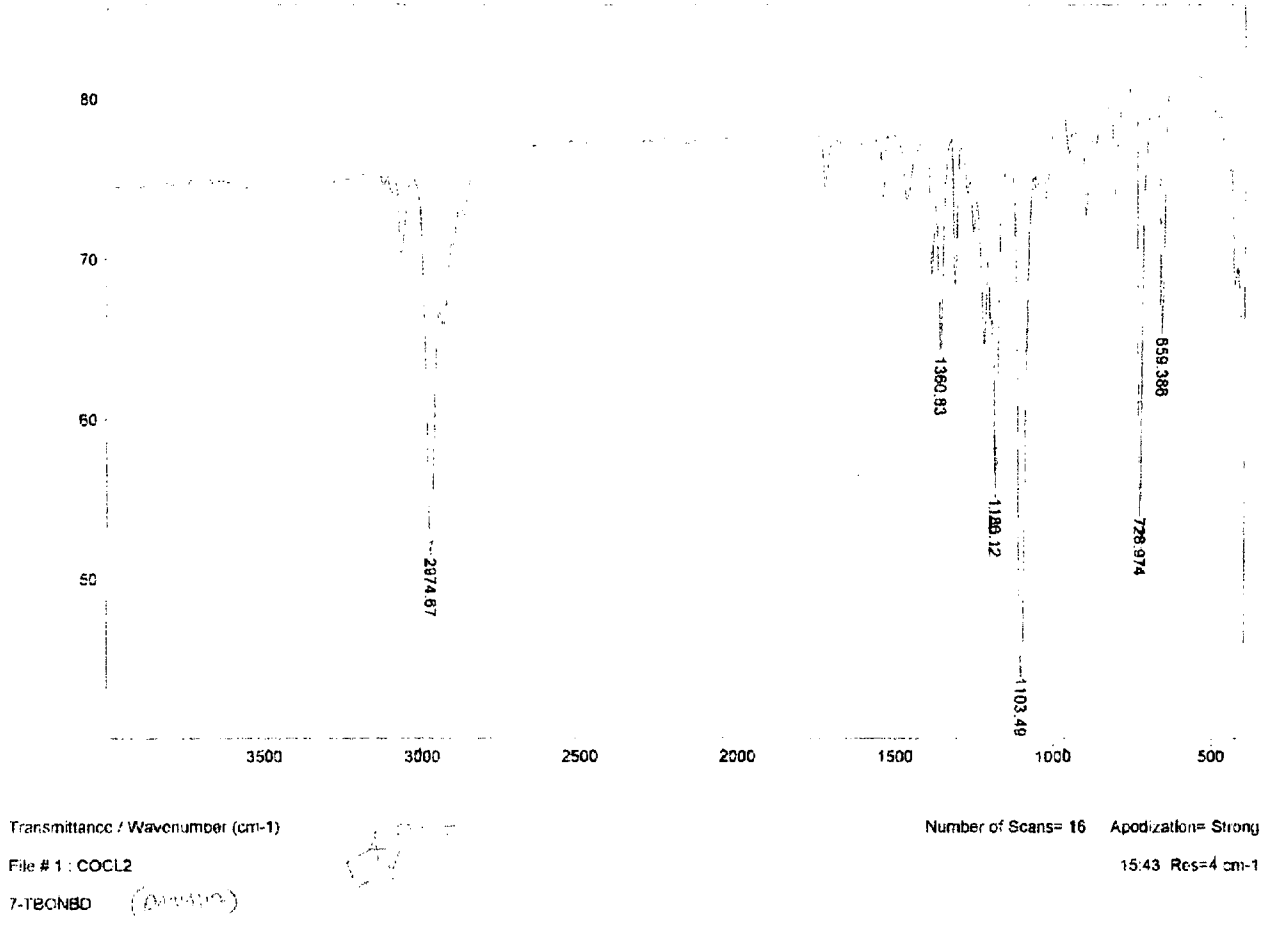

Figure A.14. Infra-red spectrum of 7-tert-butoxynorbornadiene (1)

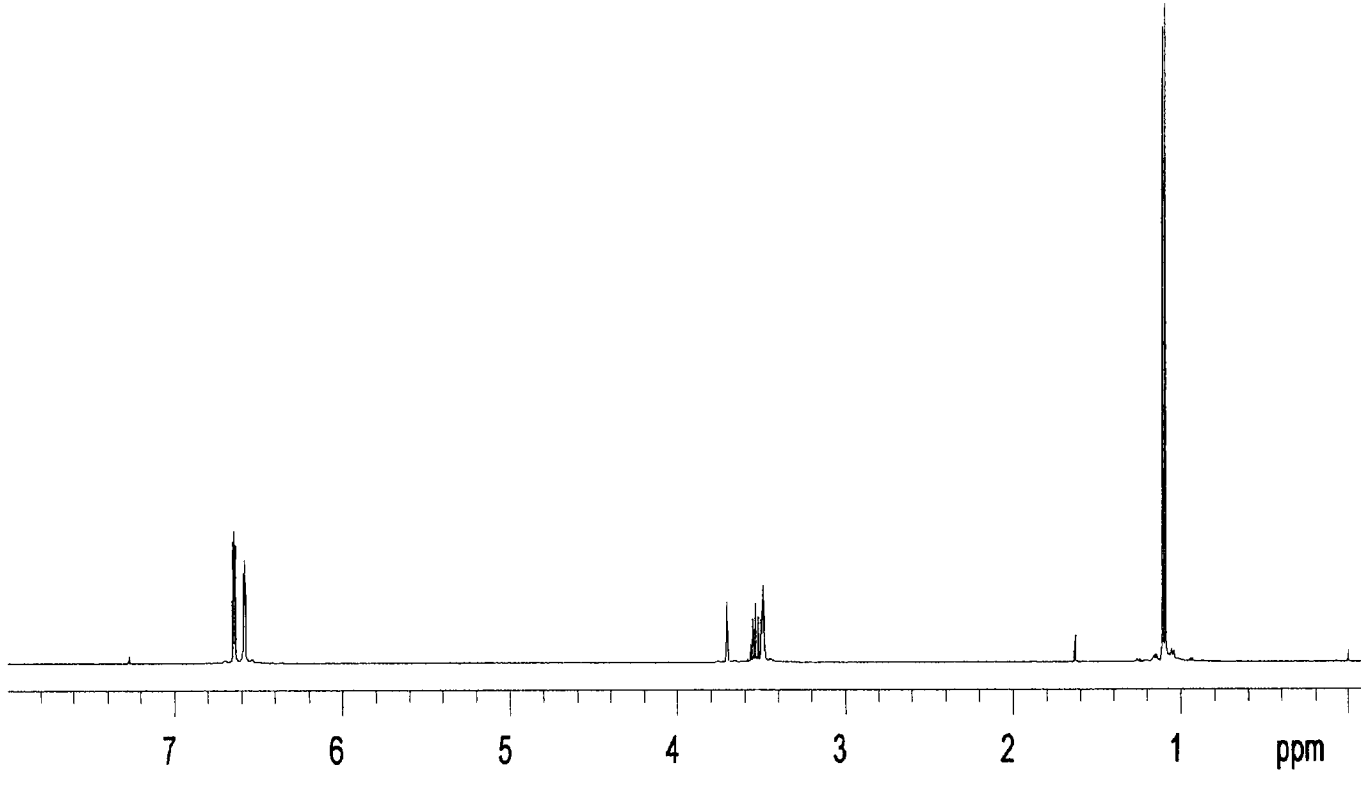

*Figure A.15. ^{1}H NMR spectrum ($CDCl_3$) of 7-iso-propoxynorbornadiene (**5**)*

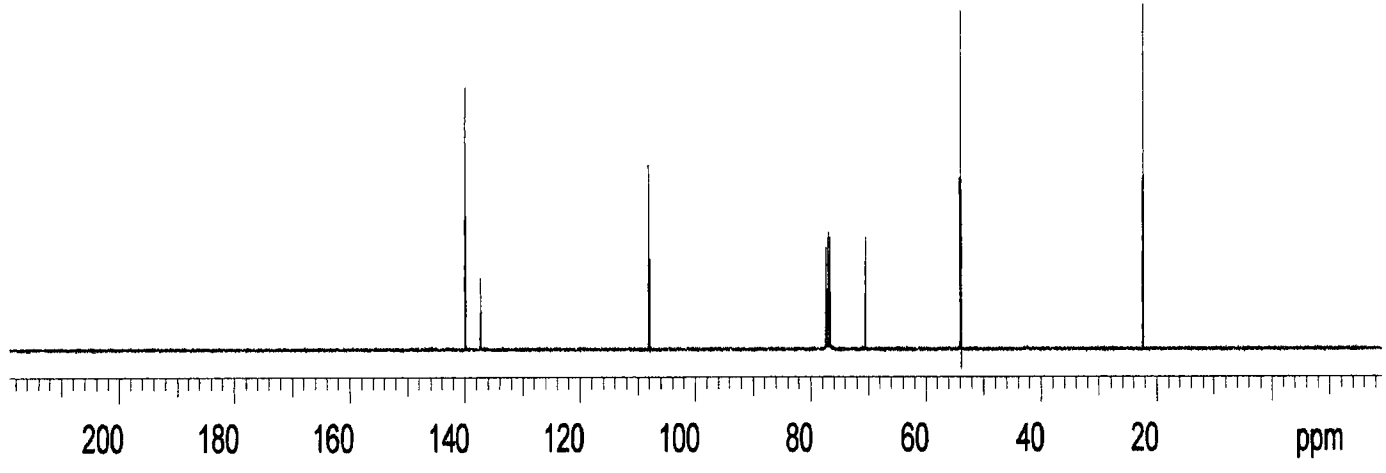

Figure A.16. ^{13}C *NMR spectrum* ($CDCl_3$) *of 7-iso-propoxynorbornadiene* (**5**)

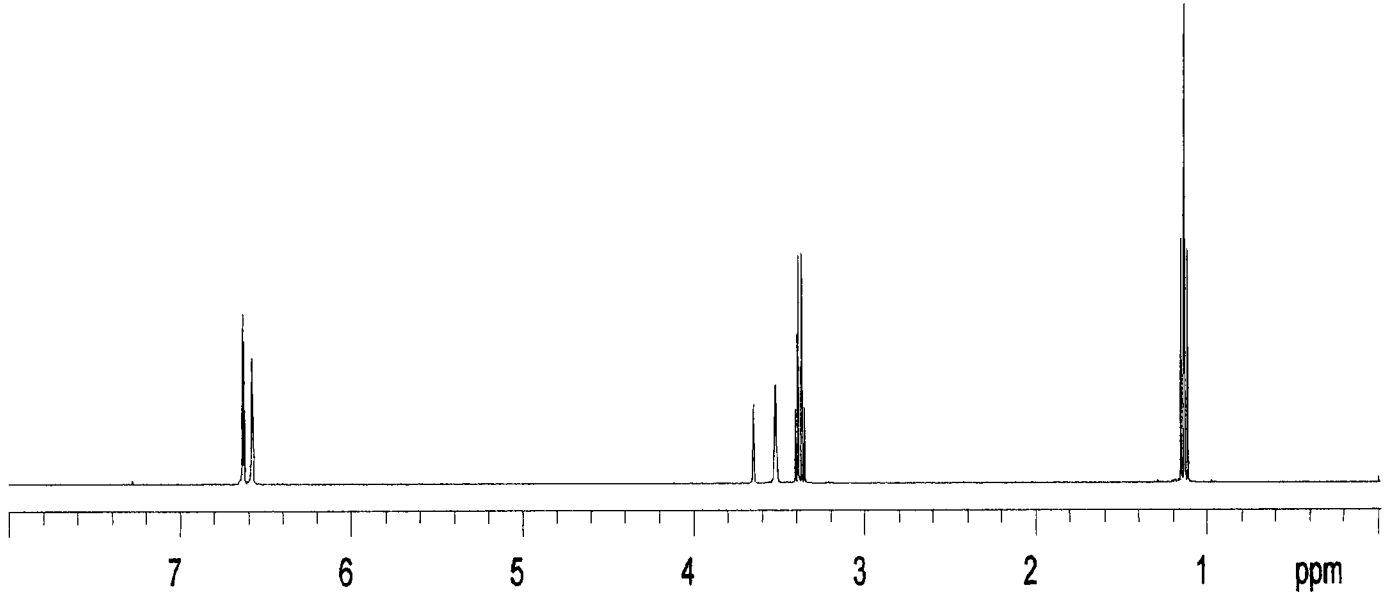

*Figure A.17. ^{1}H NMR spectrum ($CDCl_3$) of 7-ethoxynorbornadiene (**6**)*

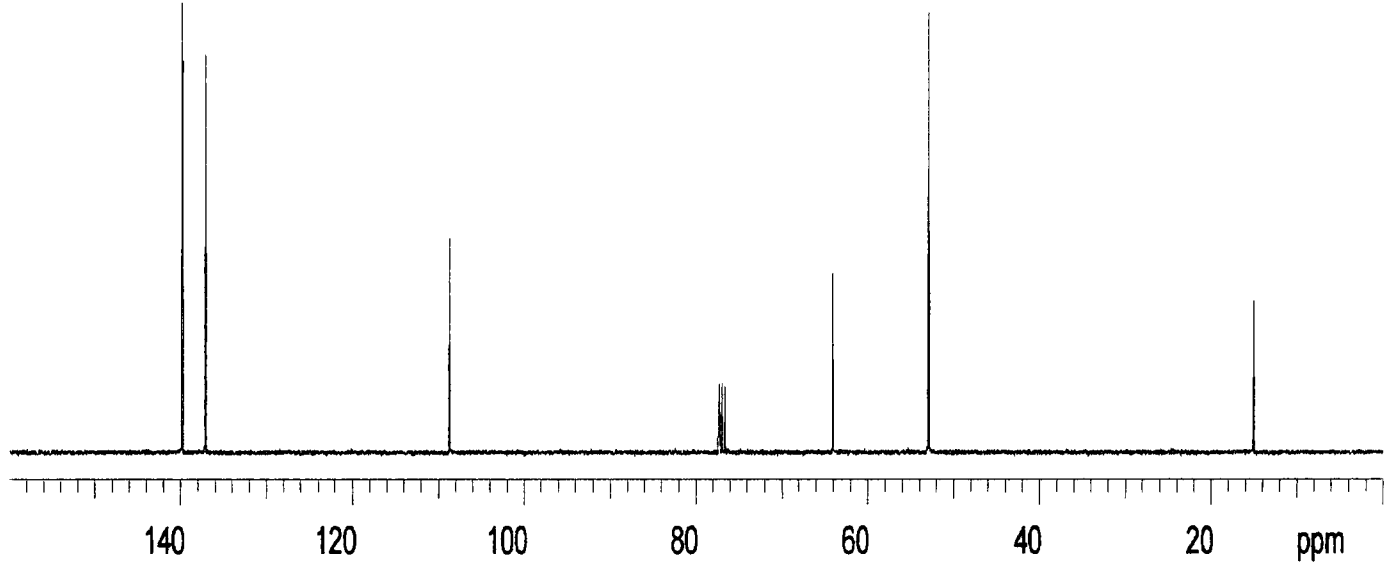

Figure A.18. ^{13}C *NMR spectrum* ($CDCl_3$) *of 7-ethoxynorbornadiene* (**6**)

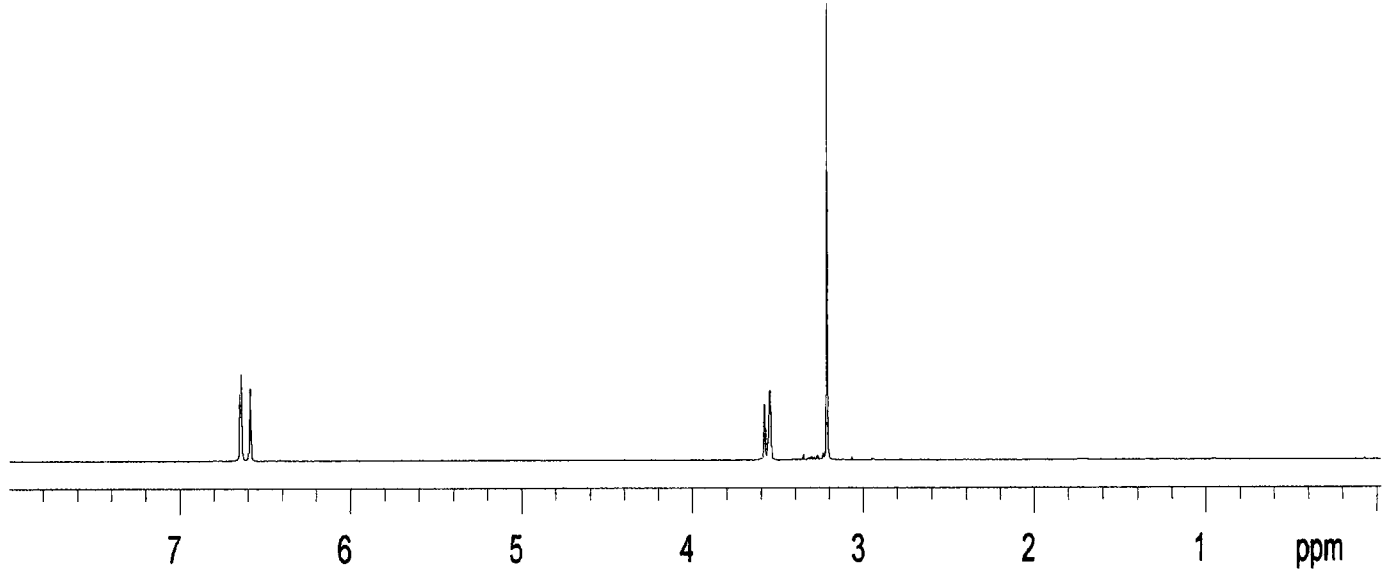

Figure A.19. ^{1}H NMR spectrum ($CDCl_3$) of 7-methoxynorbornadiene (7)

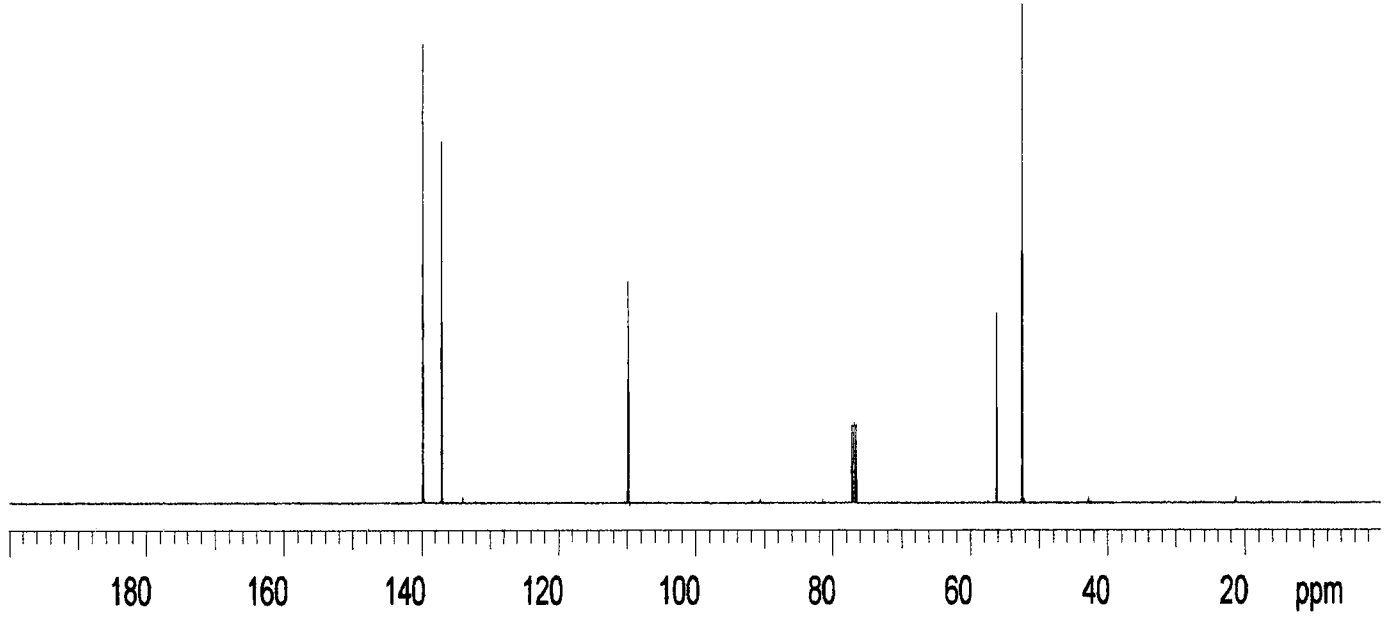

Figure A.20. ^{13}C *NMR spectrum* ($CDCl_3$) *of 7-methoxynorbornadiene (7)*

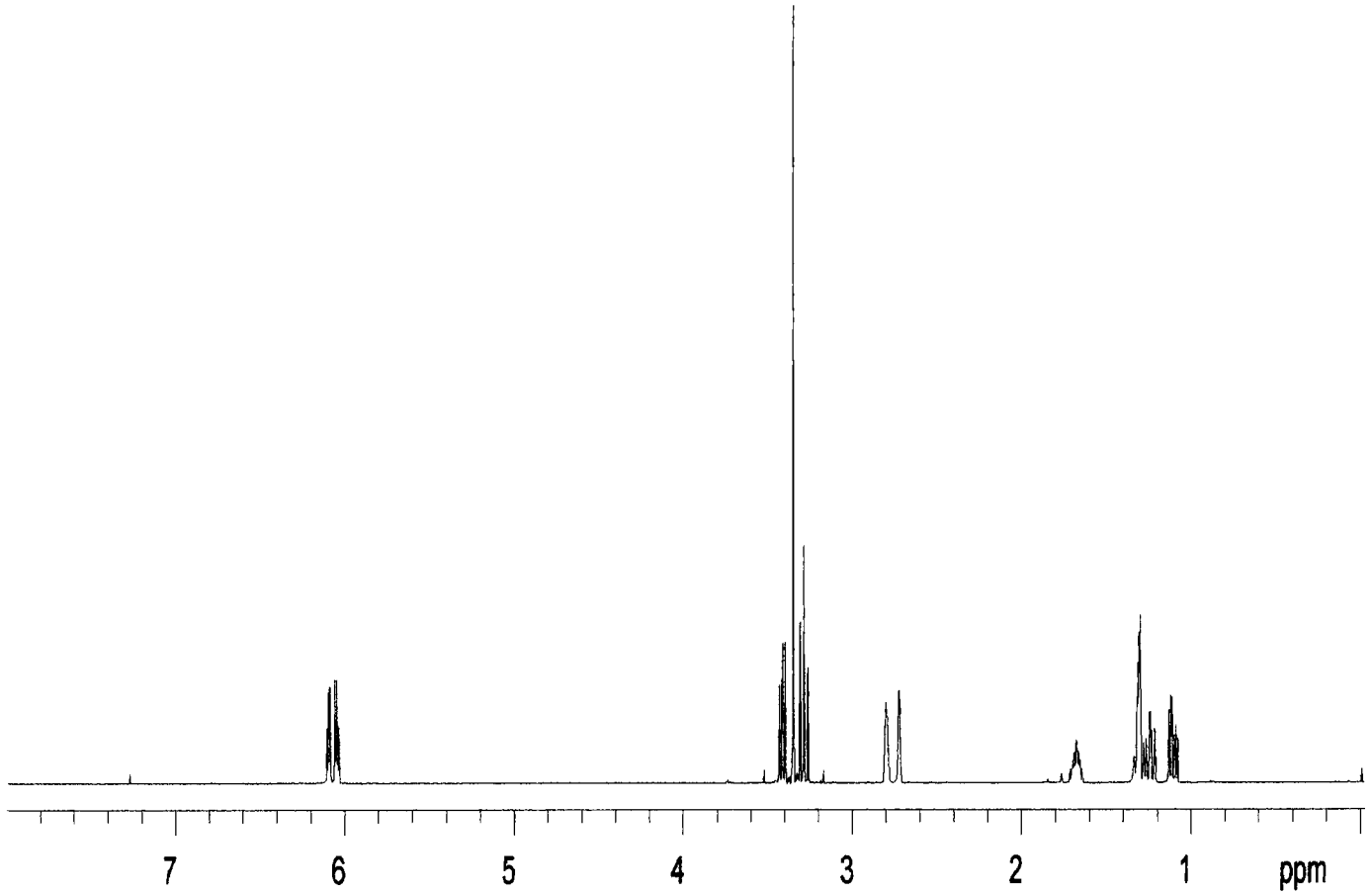

*Figure A.21. ^{1}H NMR spectrum ($CDCl_3$) of exo-5-methoxymethylnorbornene (**8**)*

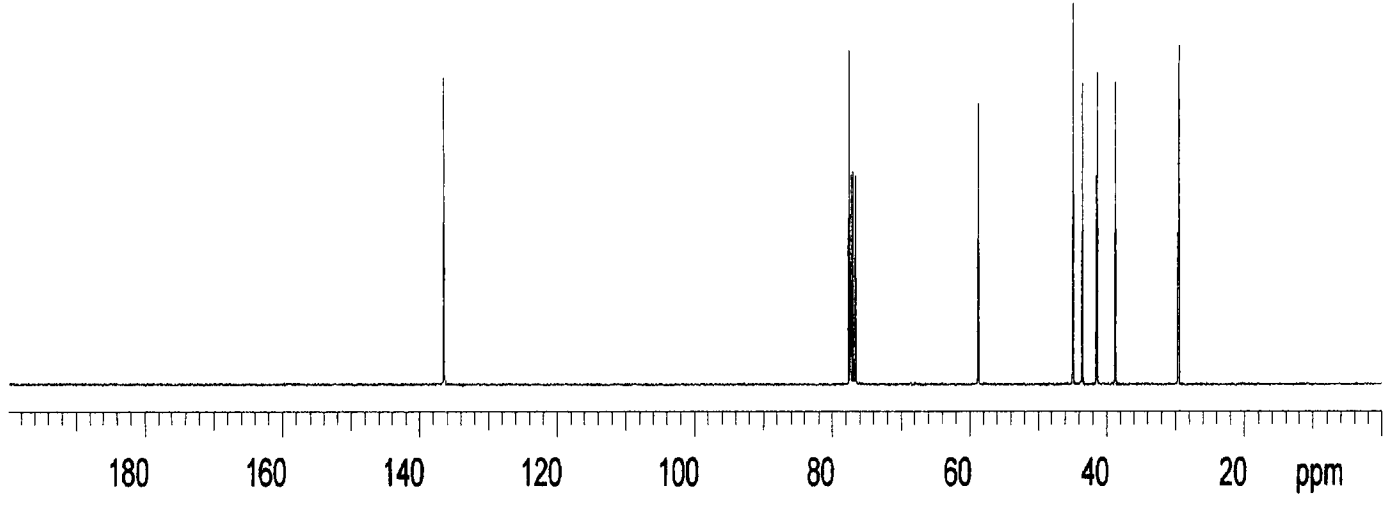

Figure A.22. ^{13}C *NMR spectrum of* ($CDCl_3$) *exo-5-methoxymethylnorbornene* ***(8)***

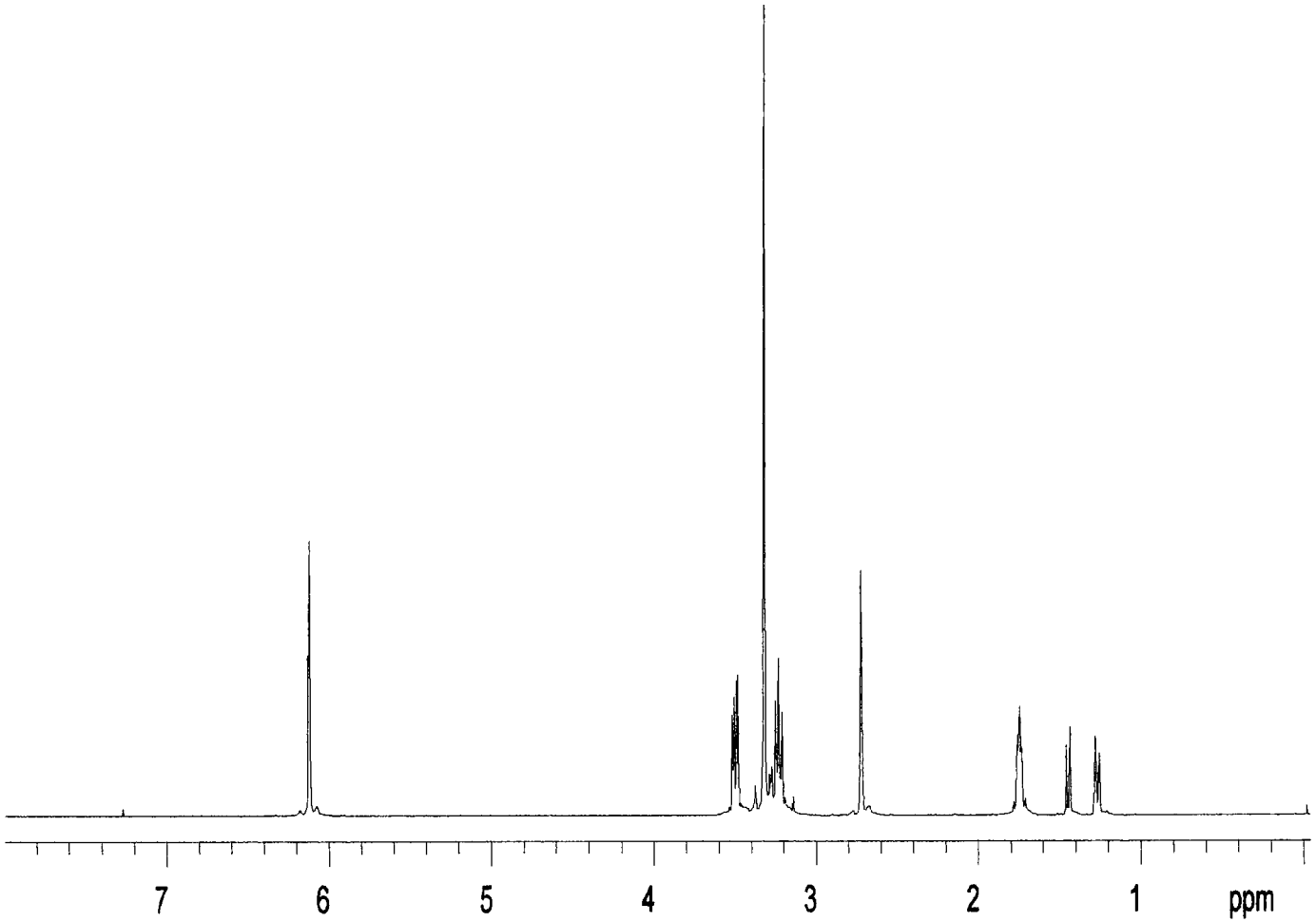

Figure A.23. ^{1}H *NMR spectrum* ($CDCl_3$) *of exo,exo-5,6-bis(methoxymethyl)norbornene (**9**)*

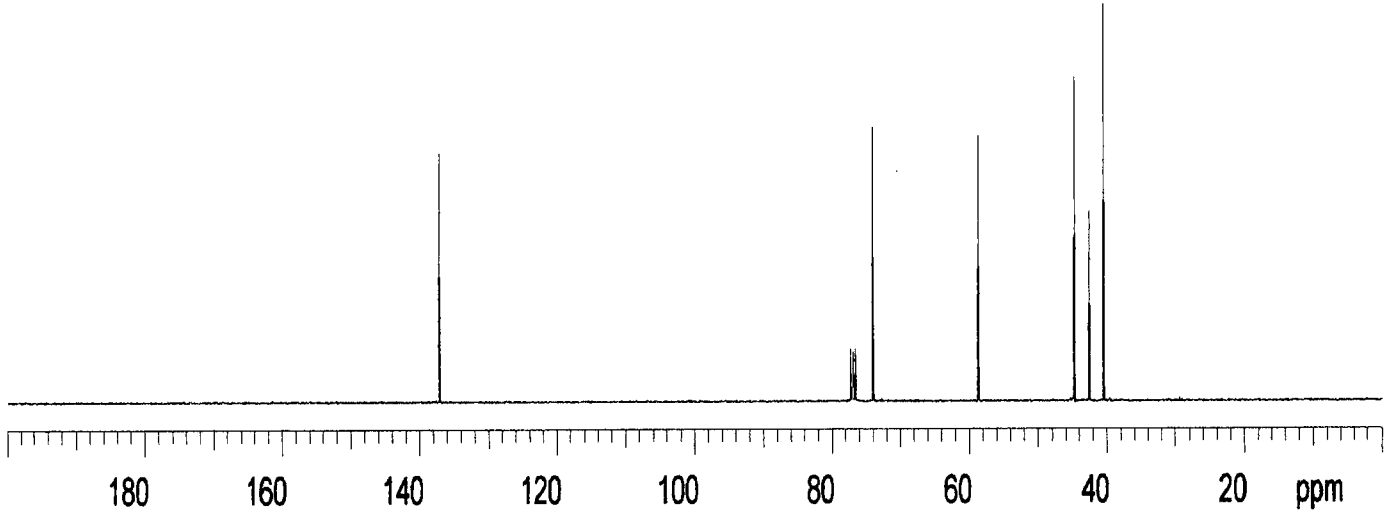

Figure A.24. ^{13}C *NMR spectrum* ($CDCl_3$) *of exo,exo-5,6-bis(methoxymethyl)norbornene* (**9**)

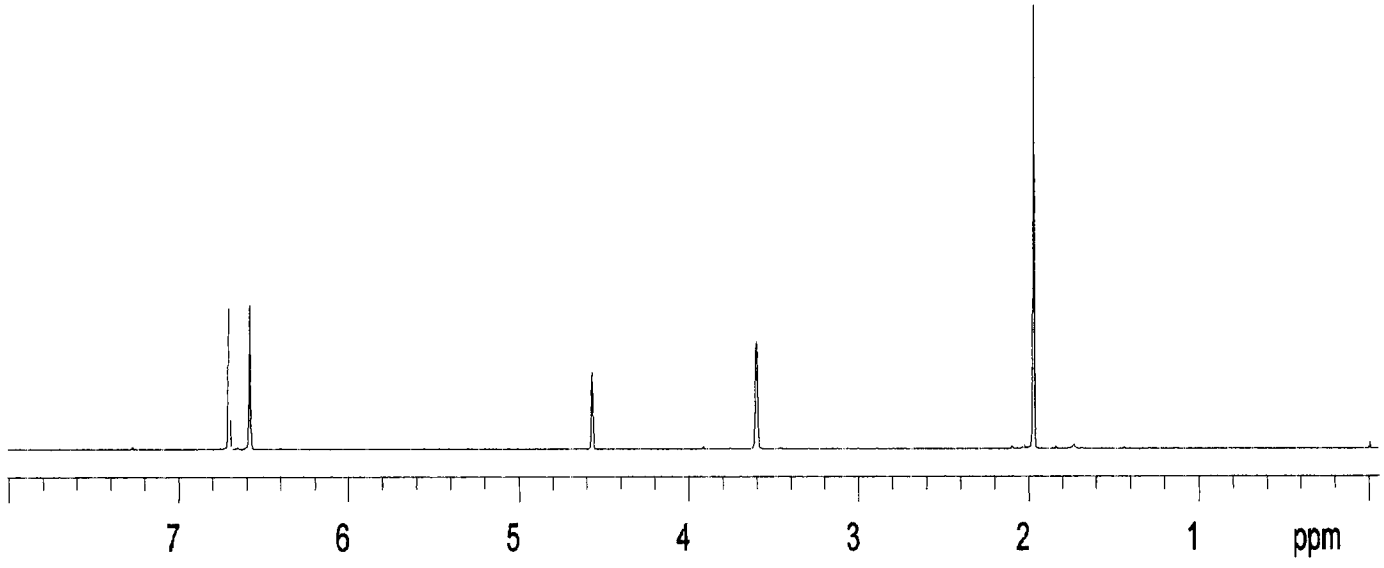

*Figure A.25. ^{1}H NMR spectrum ($CDCl_3$) of 7-acetoxynorbornadiene (**10**)*

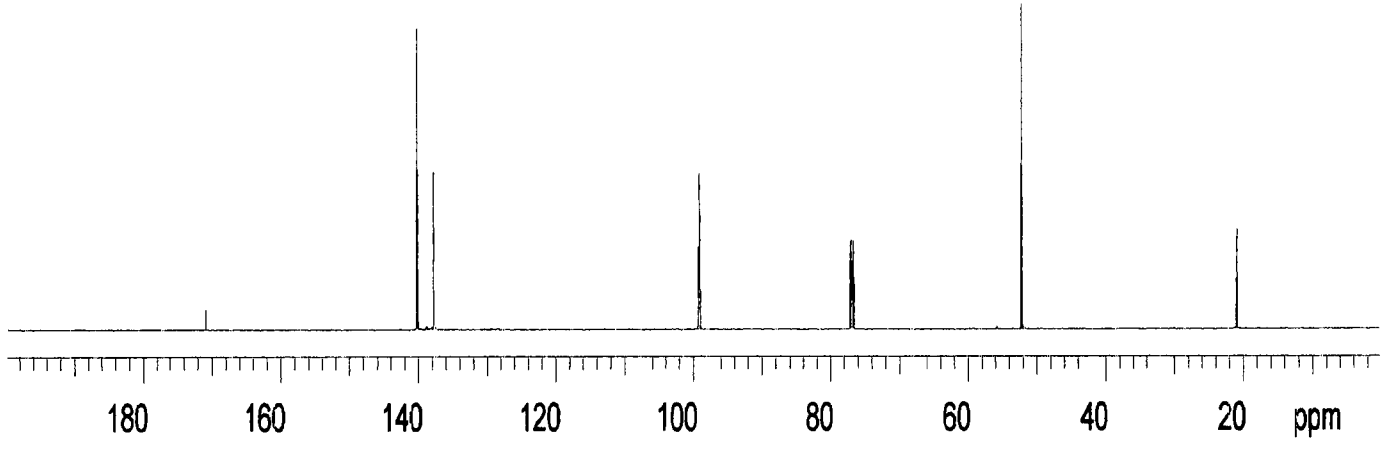

Figure A.26. ^{13}C *NMR spectrum* ($CDCl_3$) *of 7-acetoxynorbornadiene* (**10**)

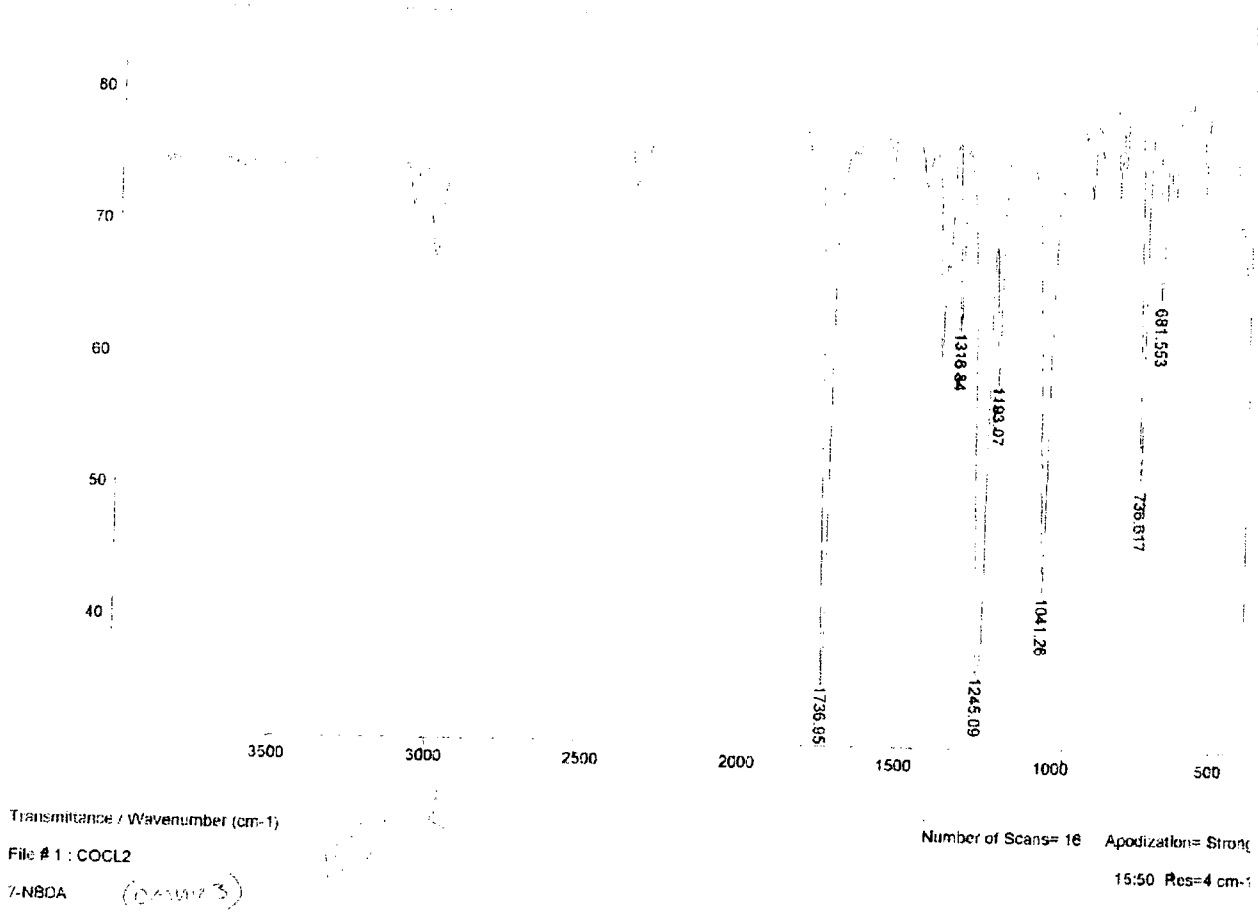

Figure A.27. Infra-red spectrum of 7-acetoxynorbornadiene ***(10)***

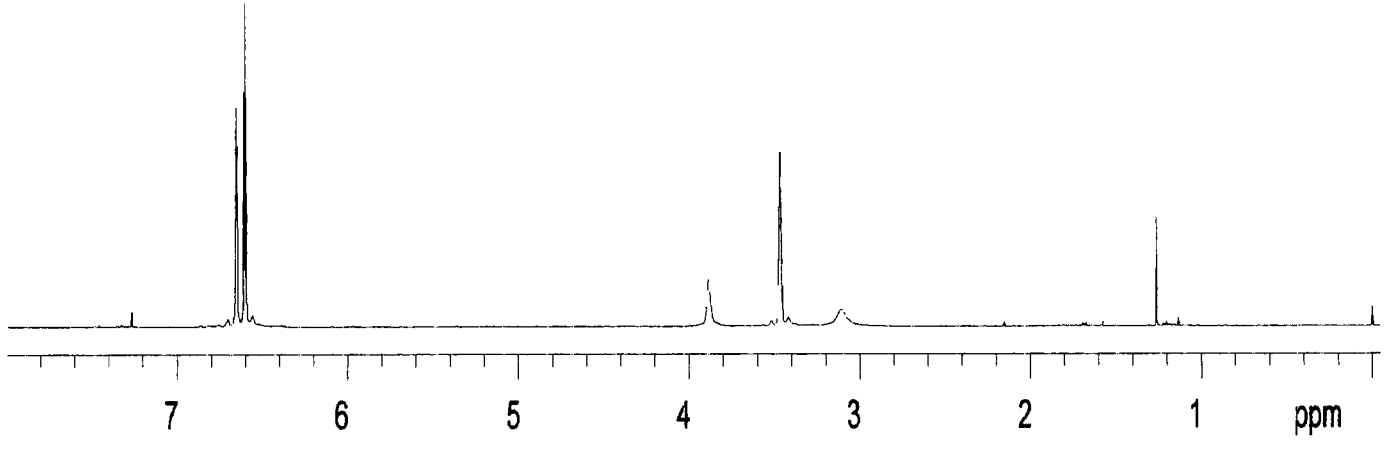

*Figure A.28. ^{1}H NMR spectrum ($CDCl_3$) of 7-hydroxynorbornadiene (**11**)*

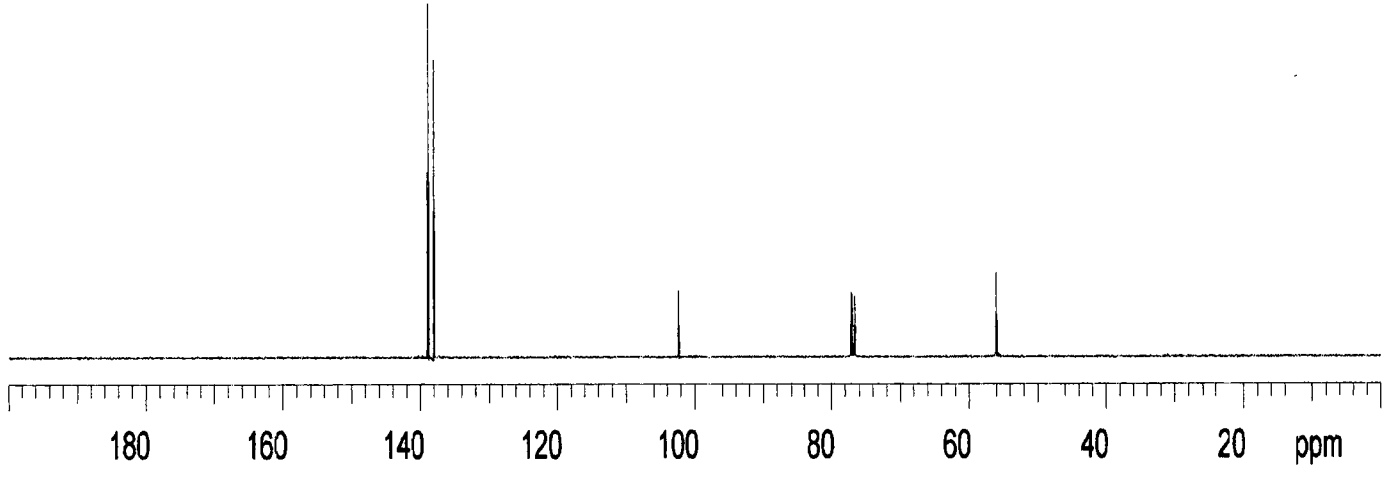

Figure A.29. ^{13}C *NMR spectrum* ($CDCl_3$) *of 7-hydroxynorbornadiene* ***(11)***

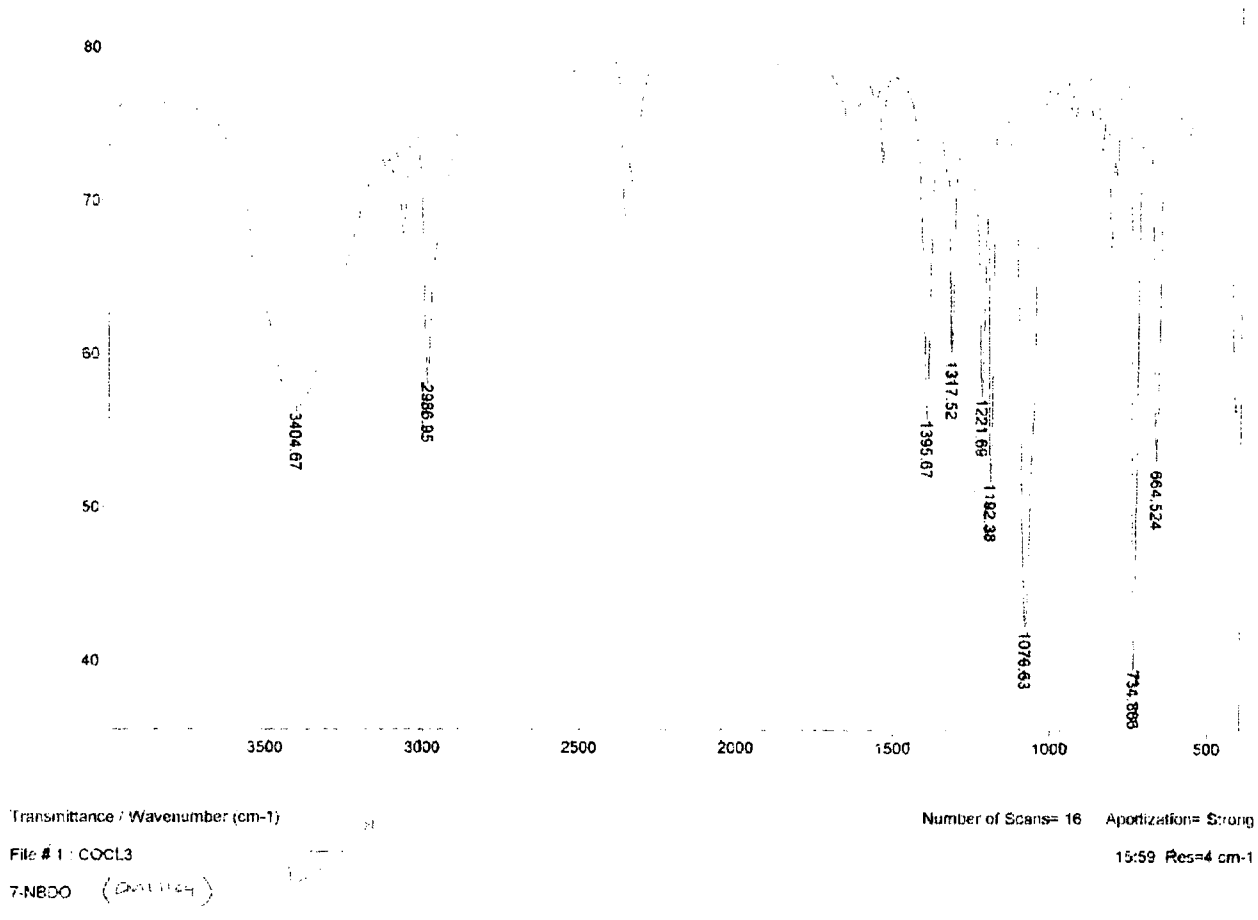

*Figure A.30. Infra-red spectrum of 7-hydroxynorbornadiene (**11**)*

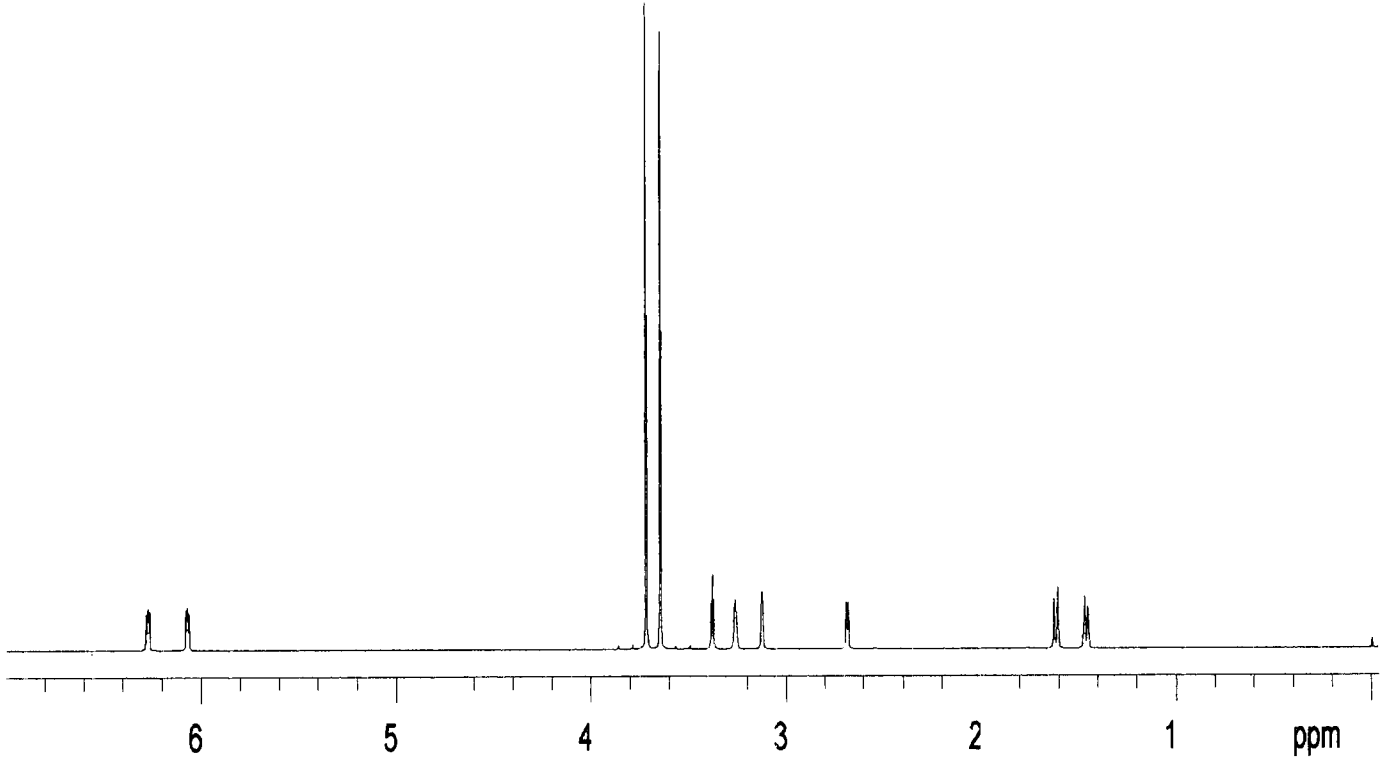

Figure A.31. ^{1}H *NMR spectrum* ($CDCl_3$) *of exo,endo-5,6-dicarbomethoxynorbornene* (**2a**)

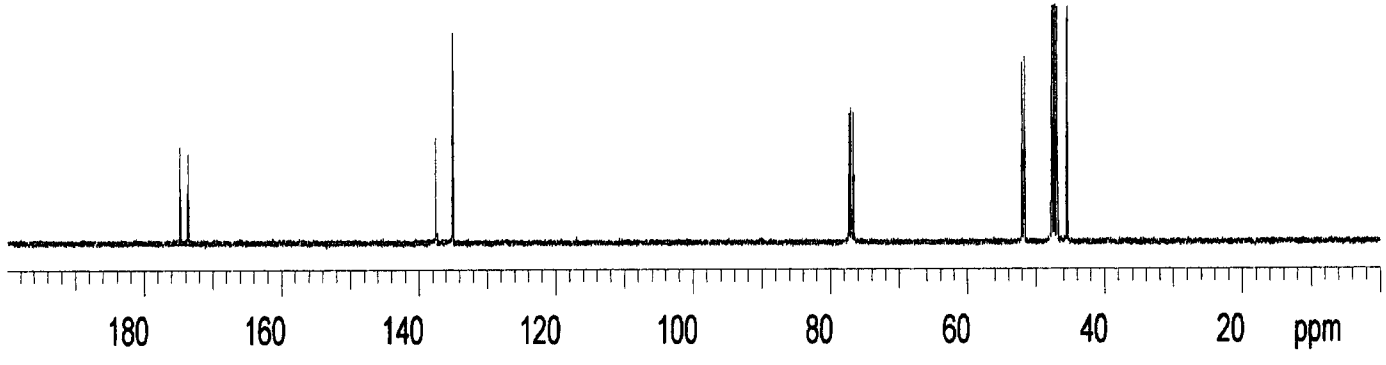

Figure A.32. ^{13}C *NMR spectrum* ($CDCl_3$) *of exo,endo-5,6-dicarbomethoxynorbornene* (**2a**)

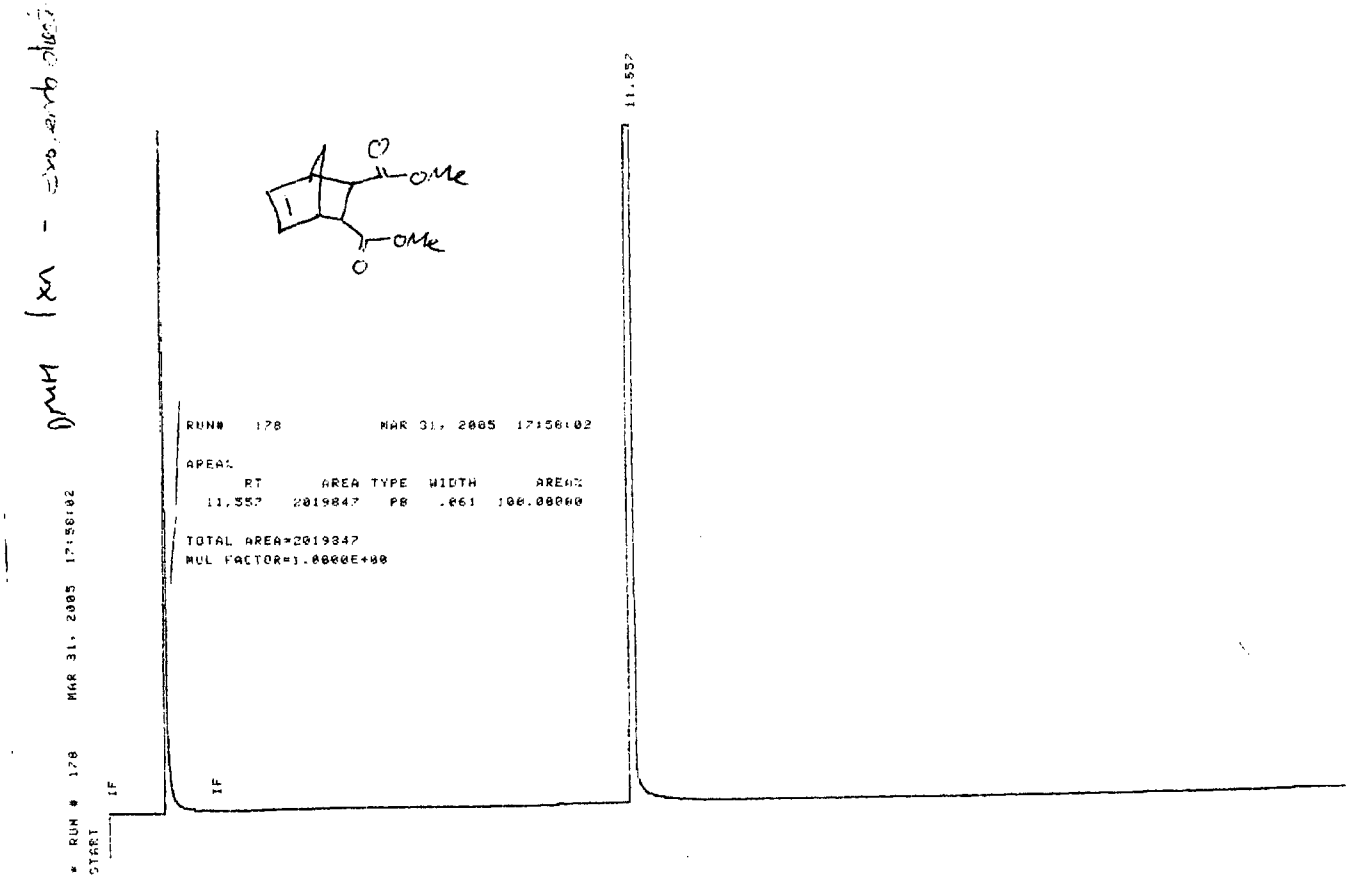

*Figure A.33. GC trace of exo,endo-5,6-dicarbomethoxynorbornene (**2a**)*

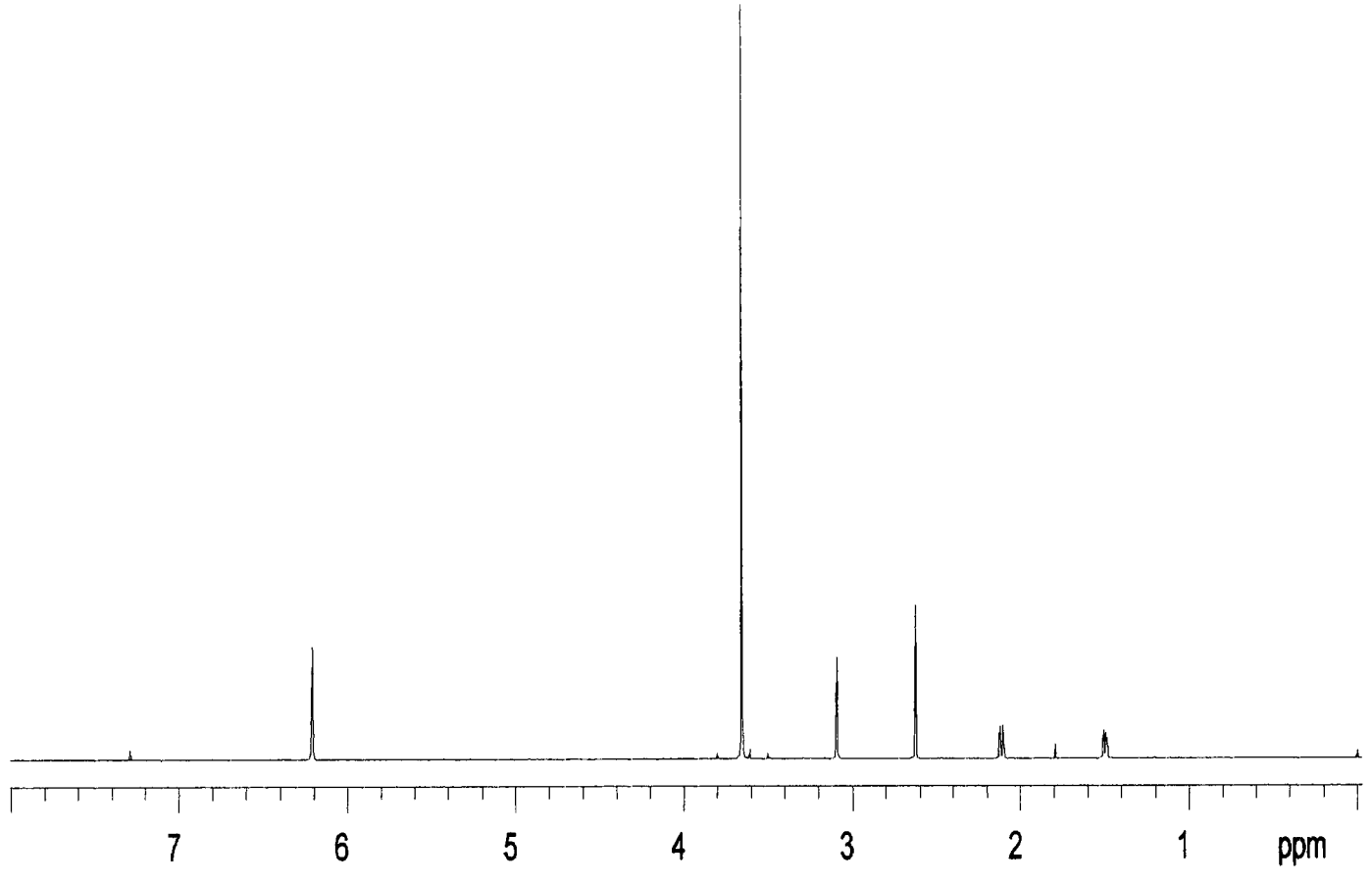

Figure A.34. ^{1}H *NMR spectrum* ($CDCl_3$) *of exo,exo-5,6-dicarbomethoxynorbornene* (**2b**)

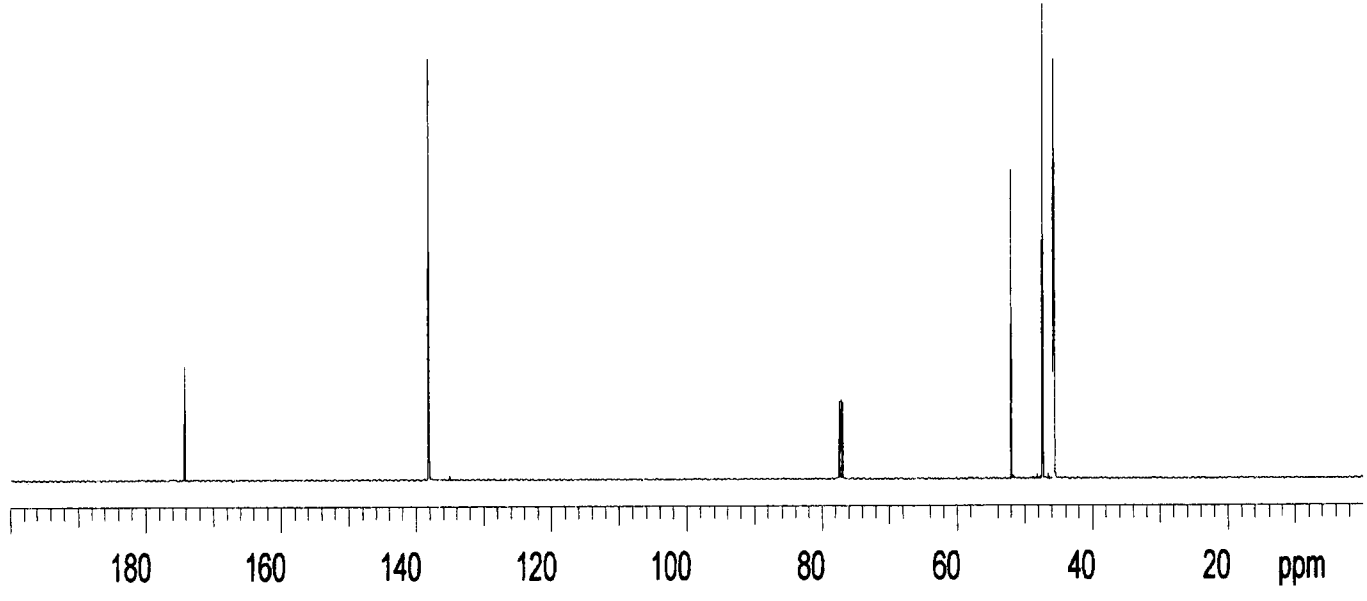

Figure A.35. ^{13}C *NMR spectrum* ($CDCl_3$) *of exo,exo-5,6-dicarbomethoxynorbornene* (**2b**)

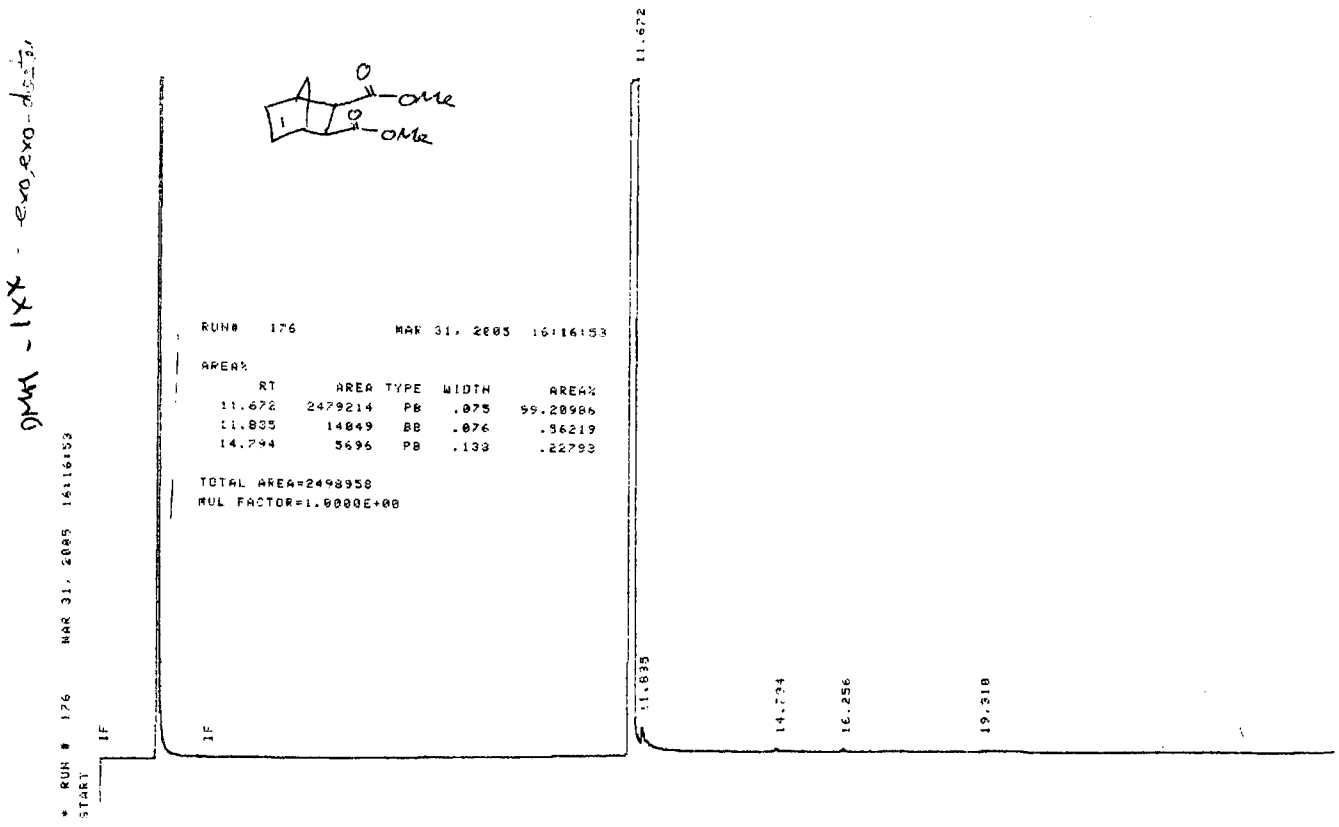

*Figure A.36. GC trace of exo,exo-5,6-dicarbomethoxynorbornene (**2b**)*

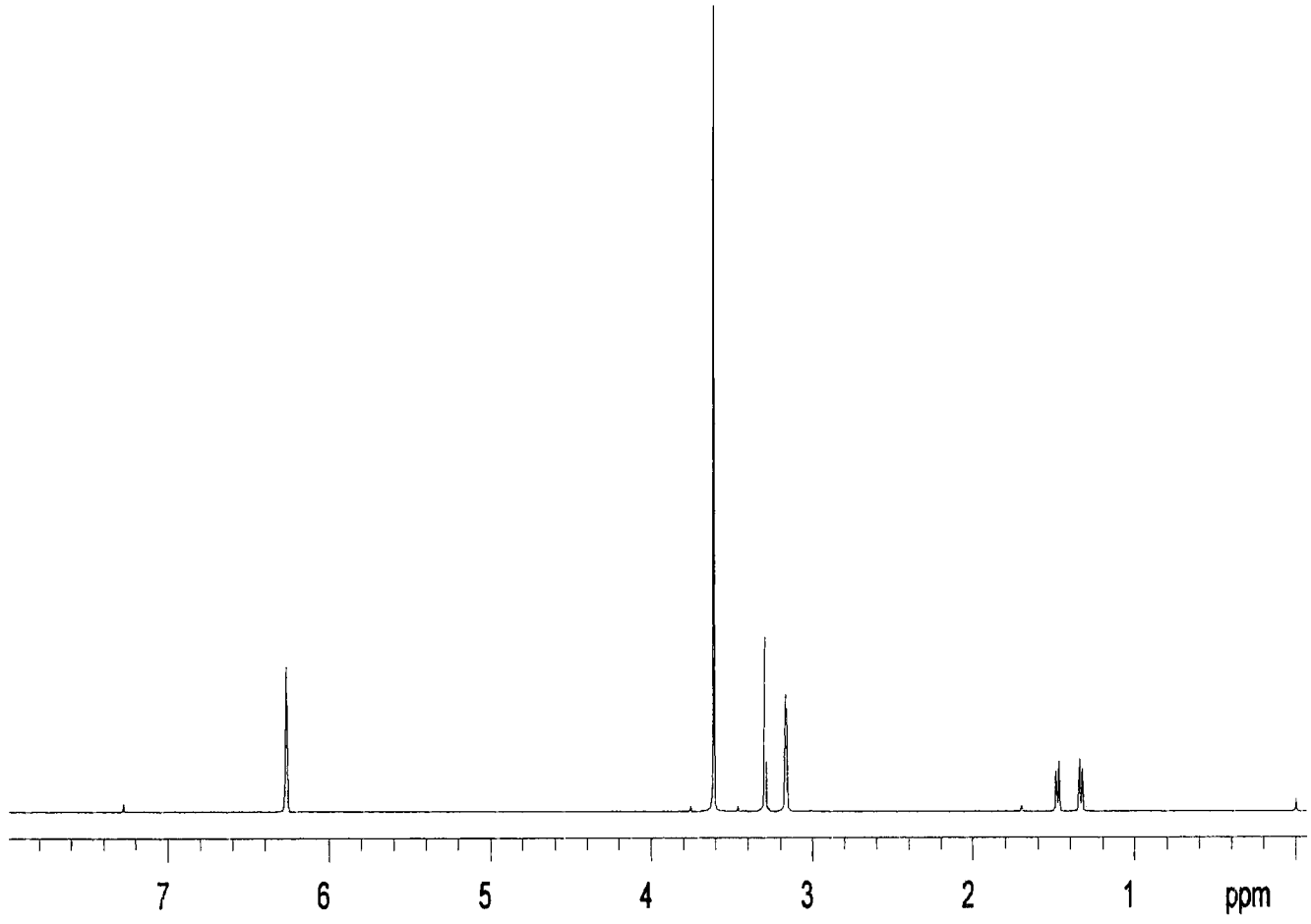

*Figure A.37. ^{1}H NMR spectrum ($CDCl_3$) of endo,endo-5,6-dicarbomethoxynorbornene (**2c**)*

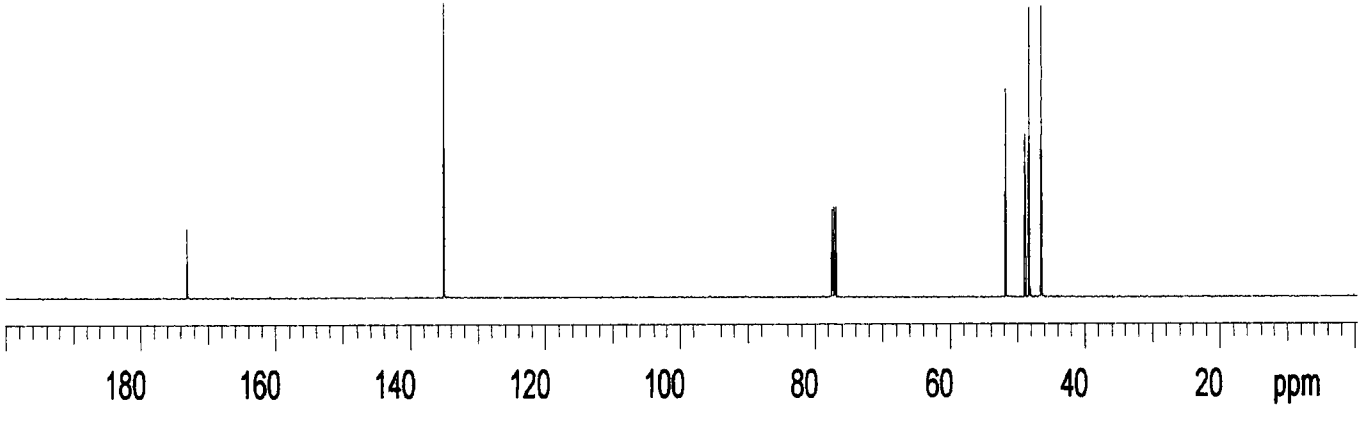

Figure A.38. ^{13}C *NMR spectrum* ($CDCl_3$) *of endo,endo-5,6-dicarbomethoxynorbornene (**2c**)*

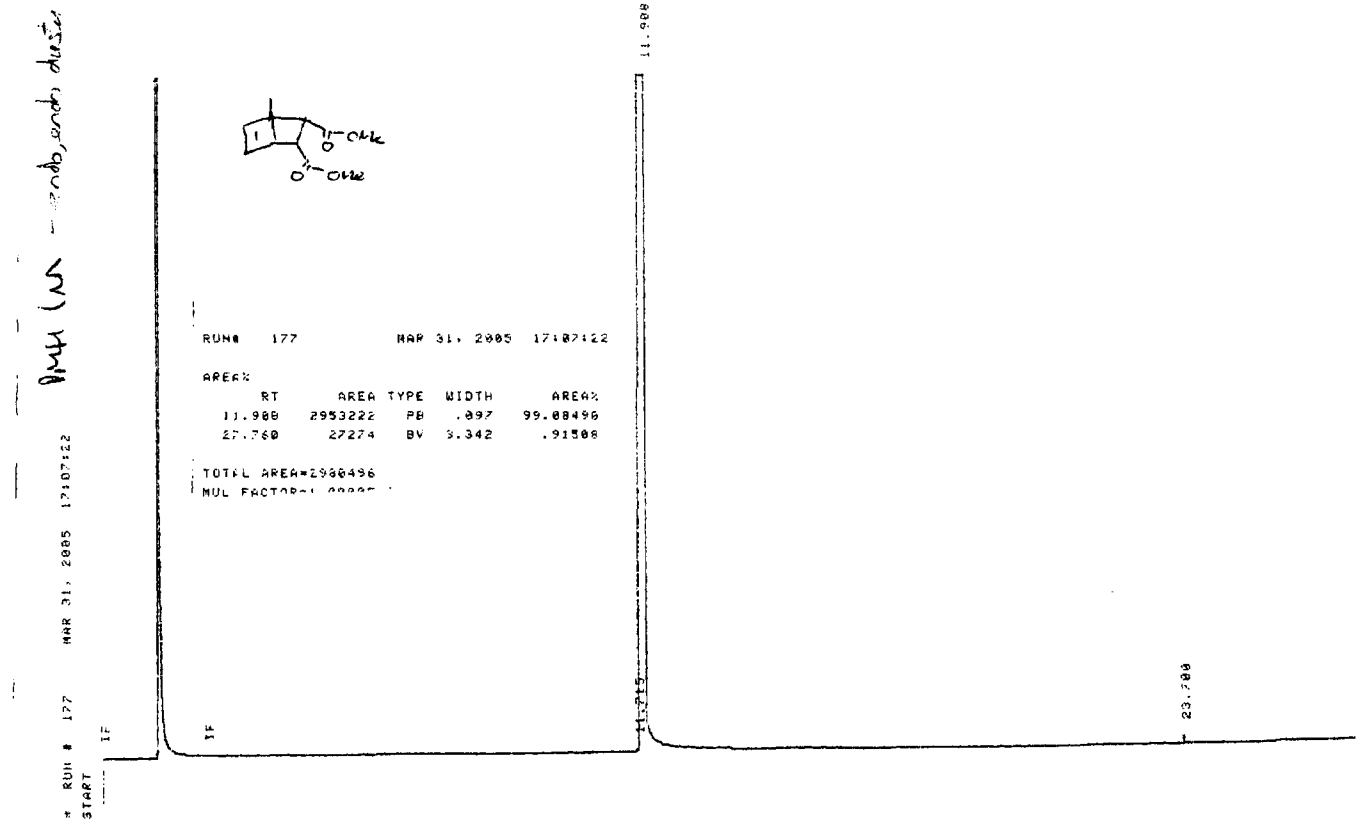

*Figure A.39. GC trace of endo,endo-5,6-dicarbomethoxynorbornene (**2c**)*

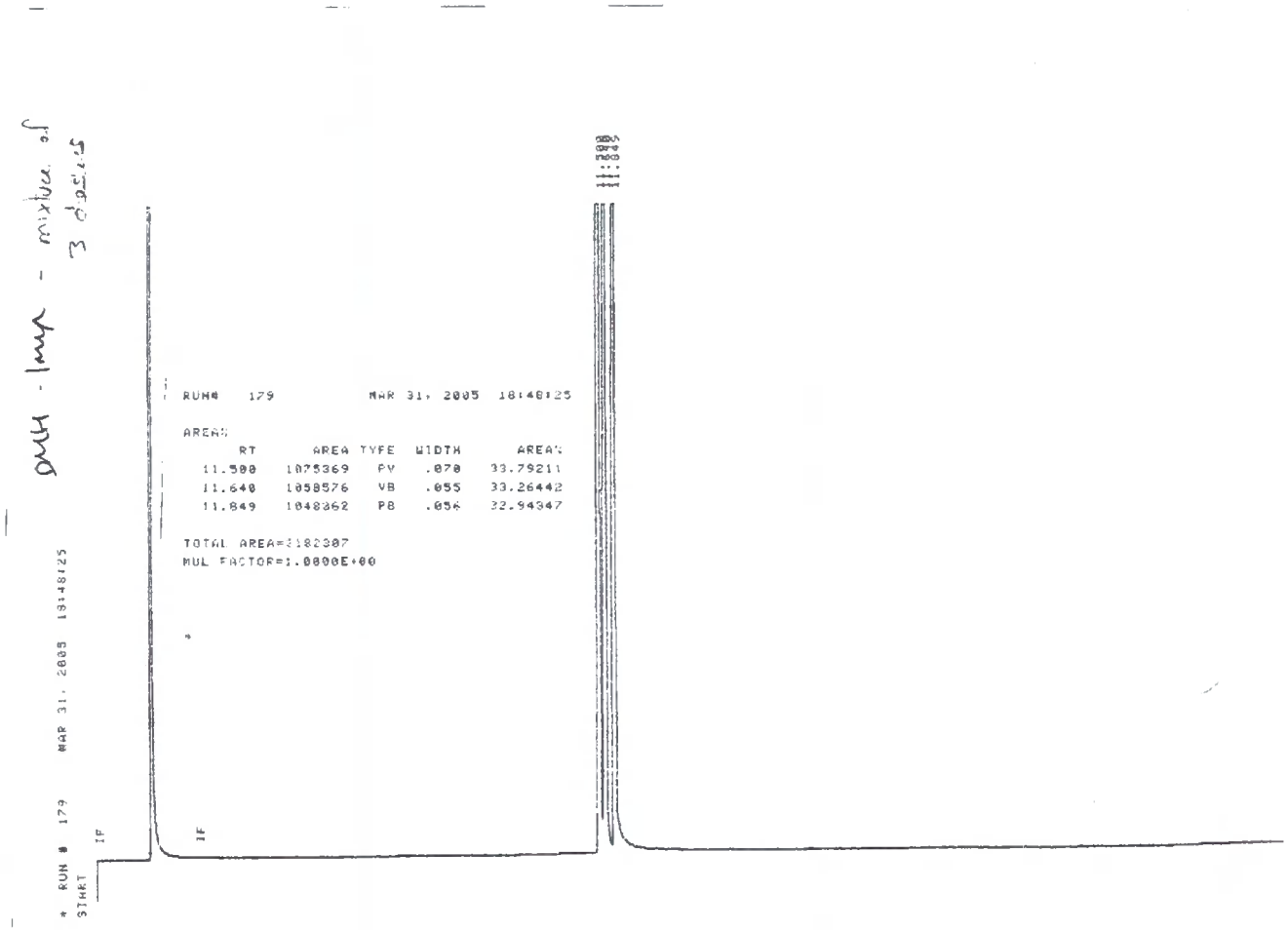

*Figure A.40. GC trace of an equimolar mixture of exo,endo-5,6-dicarbomethoxynorbornene (**2a**) , exo,exo-5,6-dicarbomethoxynorbornene (**2b**) and endo,endo-5,6-dicarbomethoxynorbornene (**2c**)*

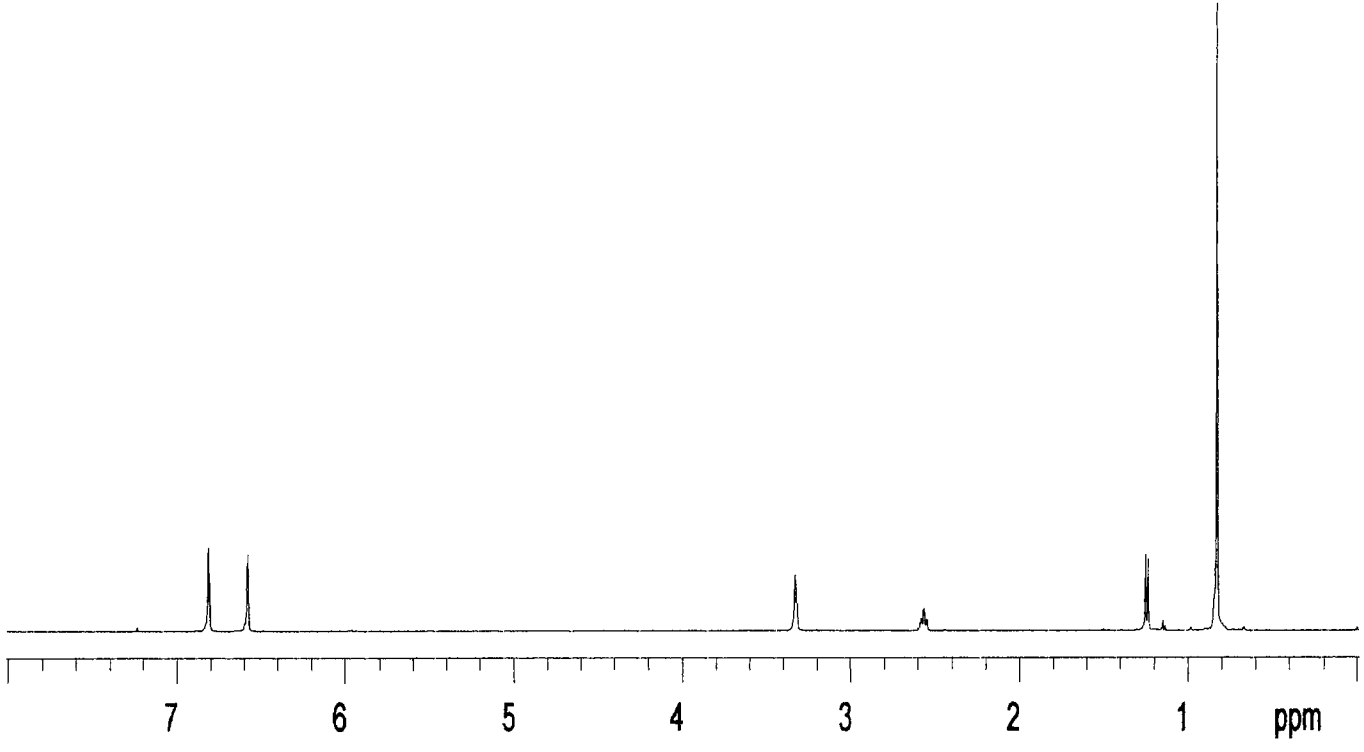

*Figure A.41. ^{1}H NMR spectrum ($CDCl_3$) of 7-neopentylnorbornadiene (**12**)*

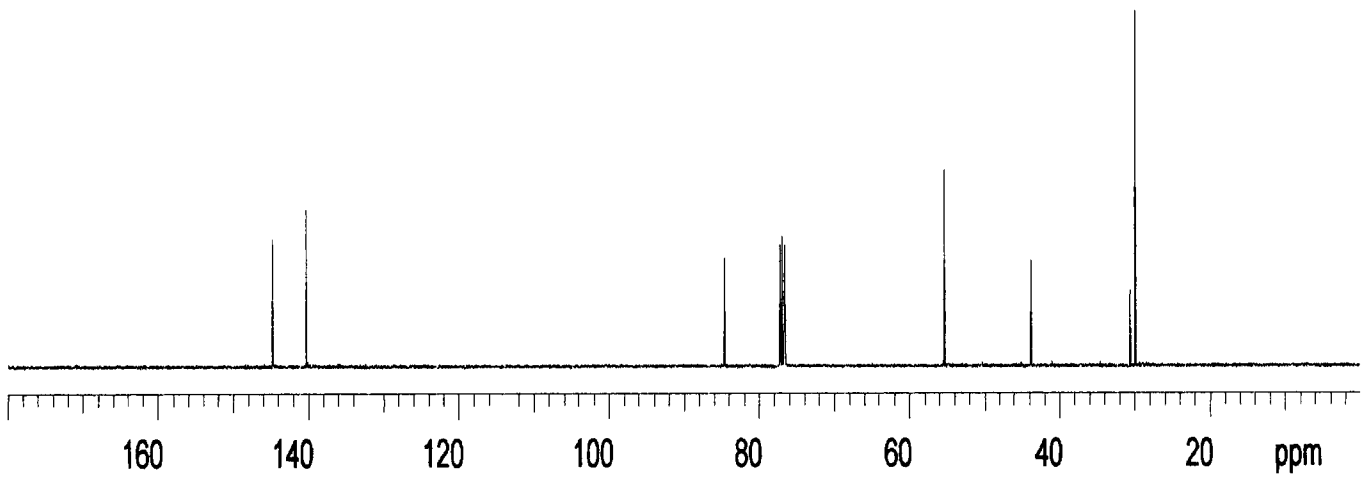

*Figure A.42 ^{13}C NMR spectrum ($CDCl_3$) of 7-neopentylnorbornadiene (**12**)*

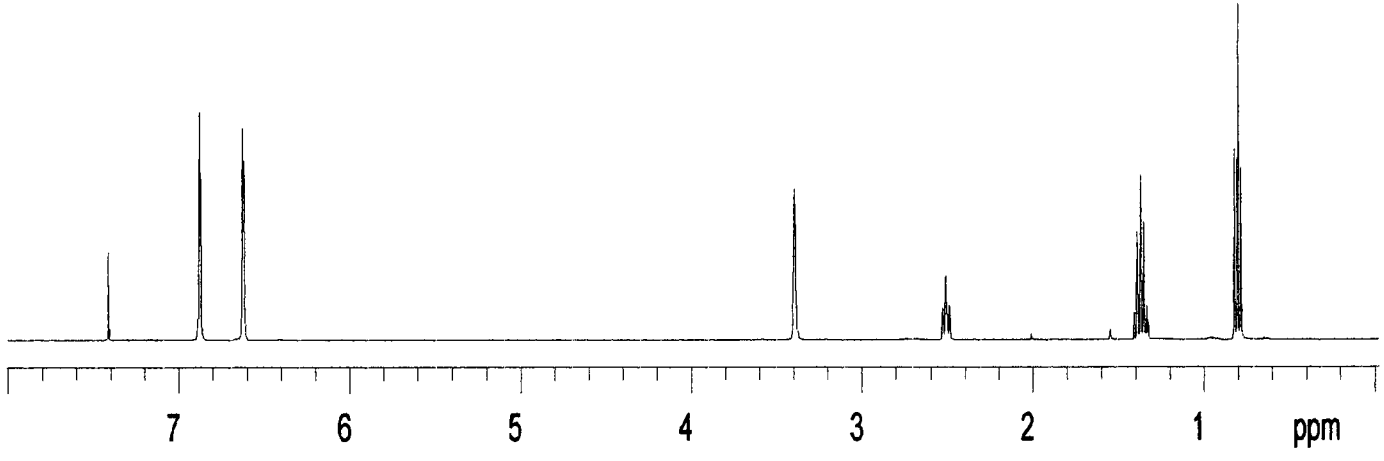

*Figure A.43. ^{1}H NMR spectrum ($CDCl_3$) of 7-ethylnorbornadiene (**13**)*

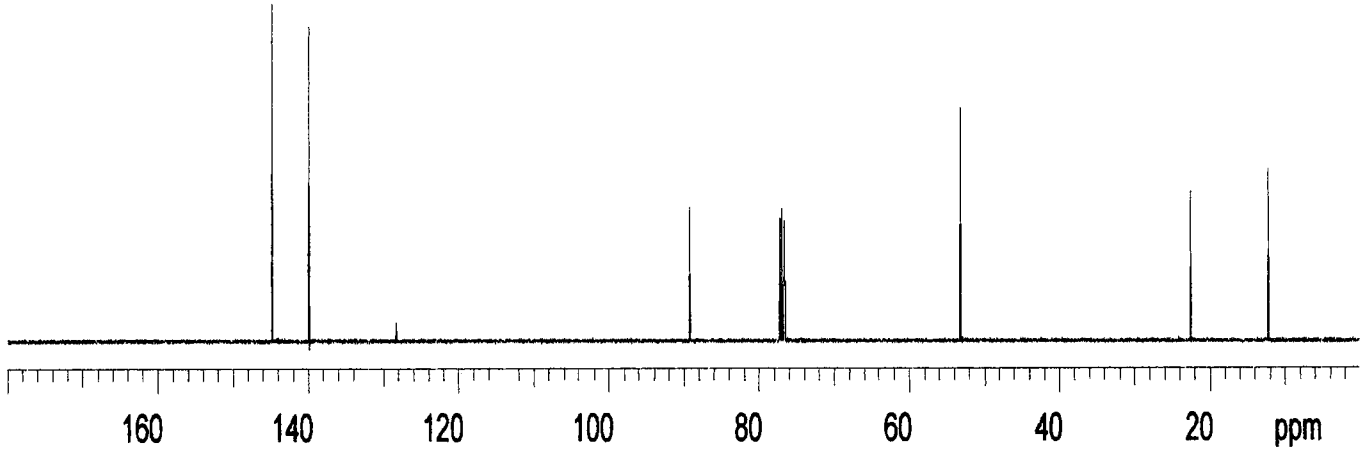

Figure A.44. ^{13}C *NMR spectrum* ($CDCl_3$) *of 7-ethylnorbornadiene* (**13**)

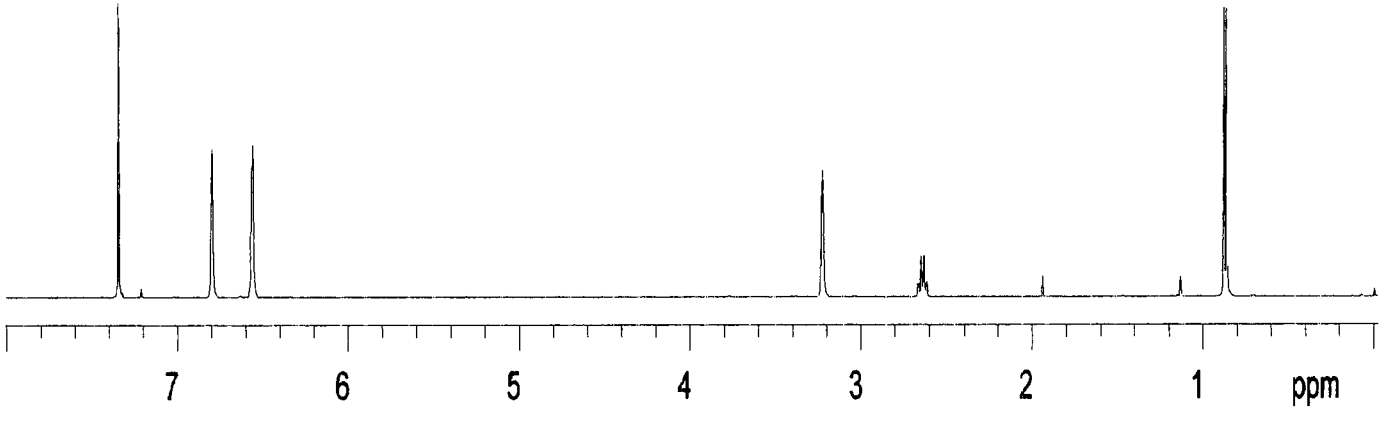

*Figure A.45. ^{1}H NMR spectrum ($CDCl_3$) of 7-methylnorbornadiene (**14**)*

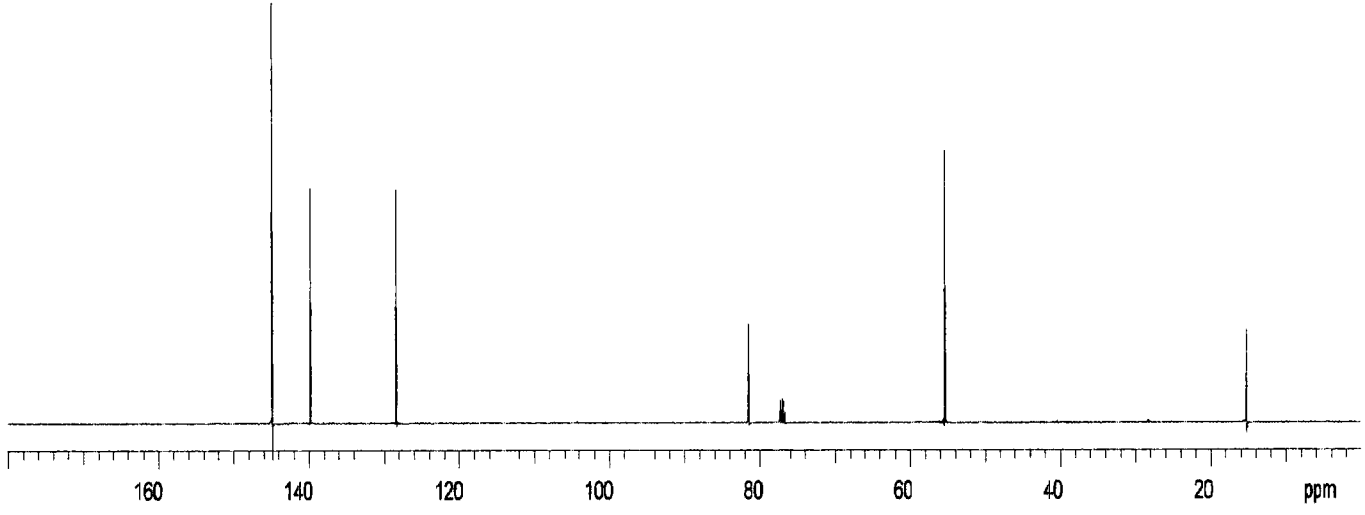

*Figure A.46. ^{13}C NMR spectrum ($CDCl_3$) of 7-methylnorbornadiene (**14**)*

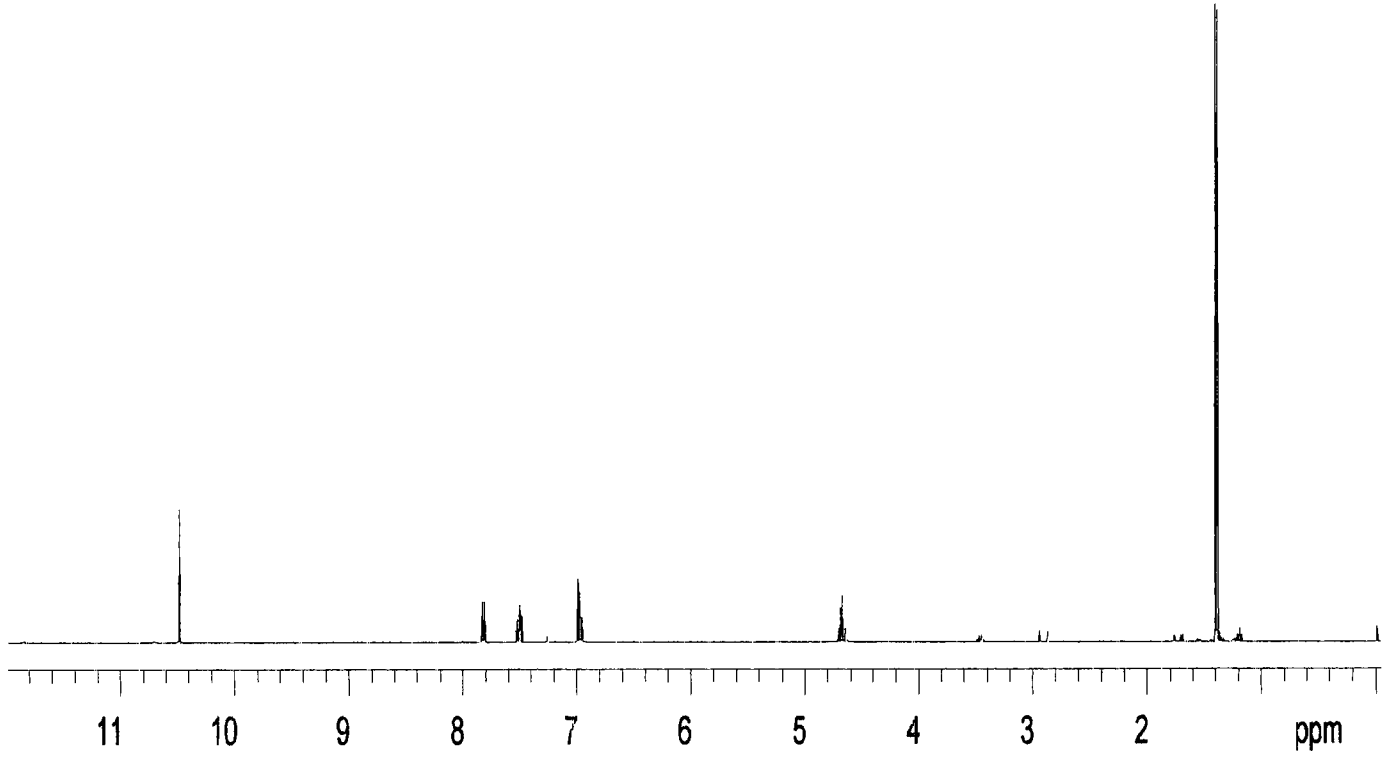

Figure A.47. ^{1}H NMR spectrum ($CDCl_3$) of 2-iso-propoxybenzaldehyde

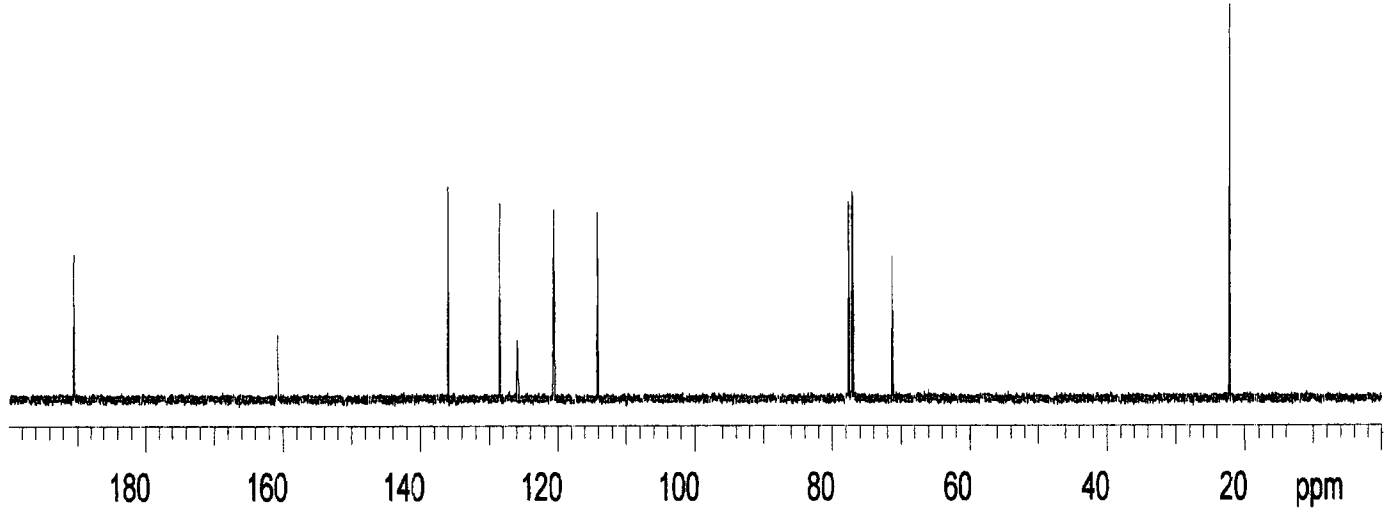

Figure A.48. ^{13}C *NMR spectrum* ($CDCl_3$) *of 2-iso-propoxybenzaldehyde*

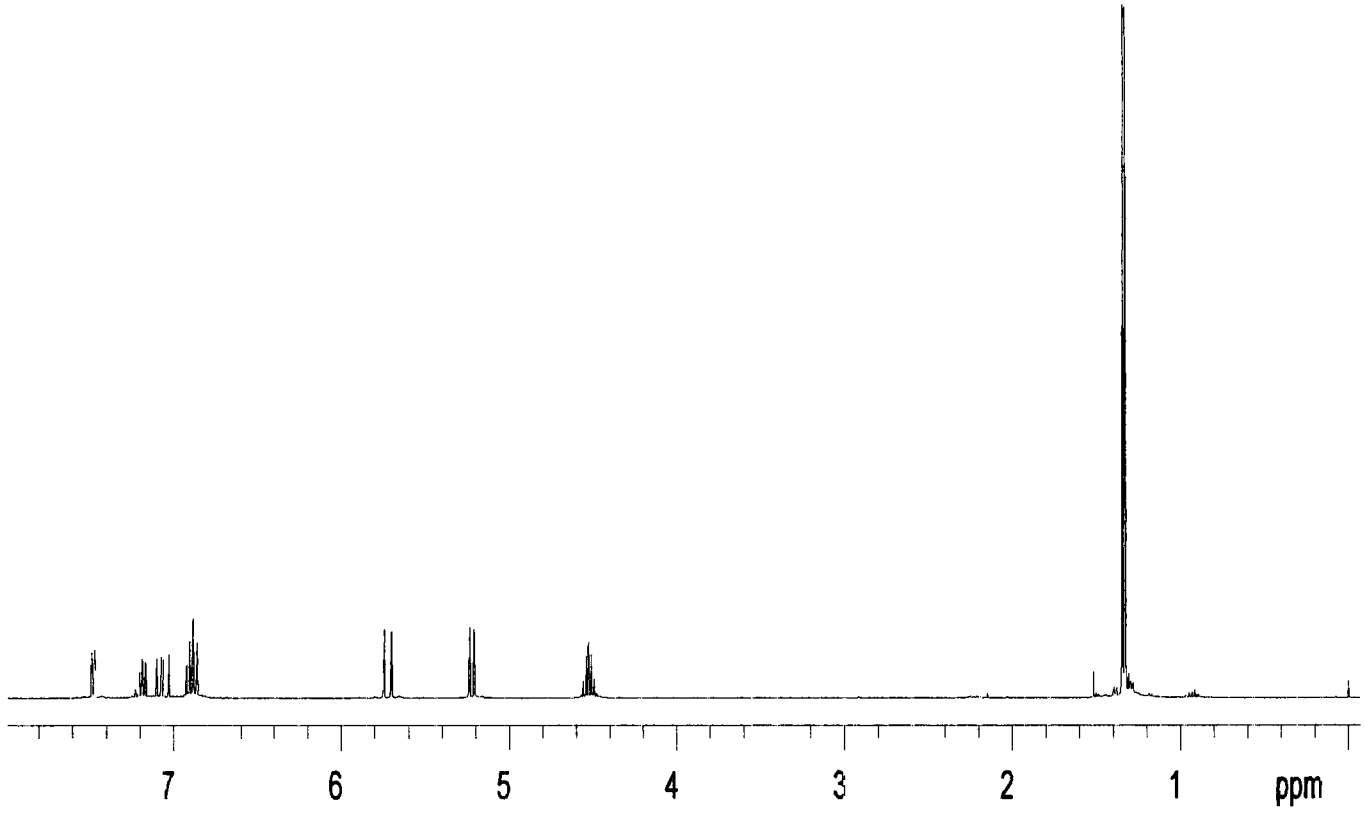

Figure A.49. ^{1}H NMR spectrum ($CDCl_3$) of 2-iso-propoxystyrene

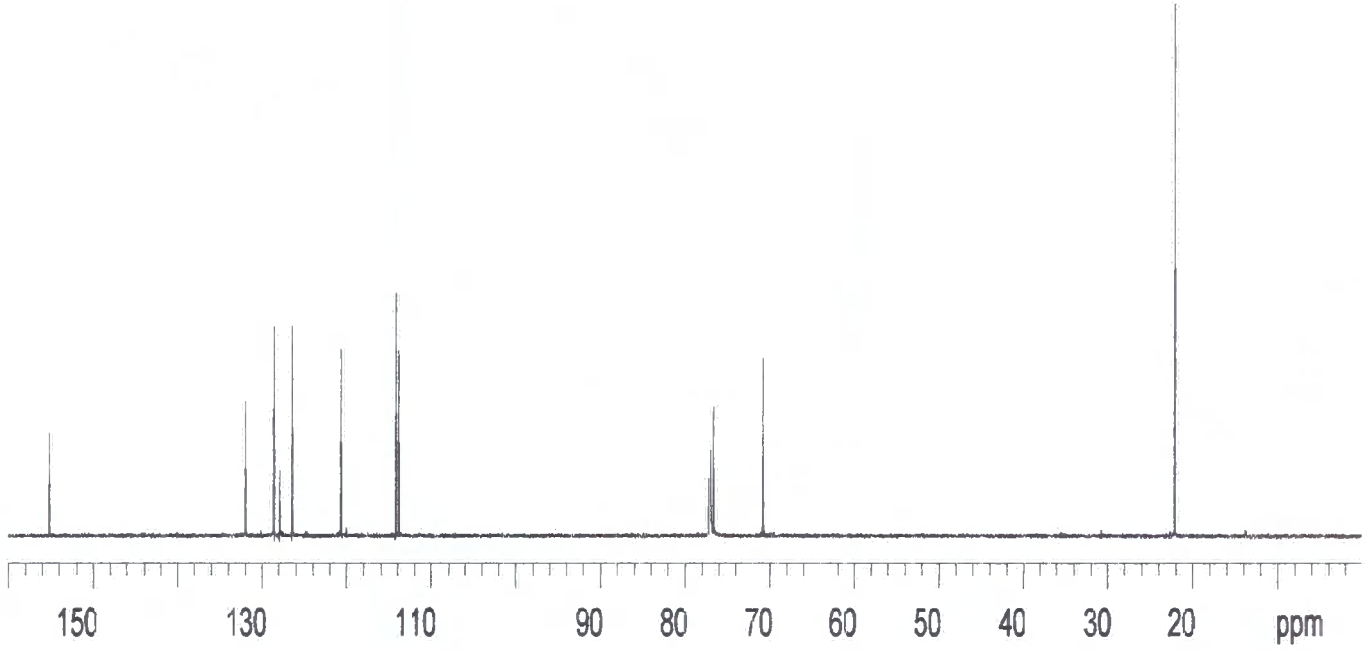

Figure A.50. ^{13}C *NMR spectrum* ($CDCl_3$) *of 2-iso-propoxystyrene*